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1, 2, 4-BUTANETRIOL: ANALYSIS AND SYNTHESIS

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RESEARCH AND TECNOLOGY DEPARTMENT

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Techniques have been developed for routine analysis of 1,2,4-butanetriol (BT) and related compounds, and a number of contaminants in commercial BT have been identified. To determine the nature and levels of contaminants that adversely affect the nitration process, trial nitrations have been run simulating actual conditions in the continuous nitration facility at the Naval Ordnance Station, Indian Head. Purification techniques were examined to improve the quality of commercially obtained BT, and several processes for BT synthesis were studied.

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FOREWORD

Techniques have been developed for routine analysis of 1,2,4-butanetriol (BT) and related compounds, and a number of contaminants in commercial BT have been identified. To determine the nature and levels of contaminants that adversely affect the nitration process, trial nitrations have been run simulating actual conditions in the continuous nitration facility at the Naval Ordnance Station, Indian Head. Purification techniques were examined to improve the quality of commercially obtained BT, and several processes for BT synthesis were studied.

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CHAPTER 1

INTRODUCTION

1,2,4-Butanetriol (BT) is a hygroscopic, water-soluble polyol whose structure immediately suggests its use as a chemical intermediate. The pure compound is a clear, colorless syrup; however, commercial material is generally straw yellow to brown. It has been described as having a sweet, burning taste but is considered non-toxic.[1] Its mass spectrum has been reported,[2] and a number of its physical properties are listed in Table 1.

1,2,4-Butanetriol is used for making the trinitrate (BTTN) which offers many advantages as a substitute for nitroglycerin (NG). Although NG is widely used as a plasticizer for nitrocellulose (NC), it presents a number of problems and replacements have been sought repeatedly. Thus, at low temperatures, NG has a tendency to crystallize in double-base formulations, causing the propellant to crack. As a result of this, recent qualification tests of a new smokeless formulation failed during temperature cycling.[6] Partial replacement of the NG by BTTN eliminated the problem.[7] Other similar evaluations have been made both in the United States and in Germany since the days of World War II.[8,9,10]

Compared to NG, BTTN has a lower freezing point, is six times less volatile, and is substantially less shock sensitive and thermally more stable. Its safety characteristics are similar to those of metriol trinitrate (MTN), another NG substitute; however, it is considerably more energetic.[11,12] Tables 2, 3, and 4 list a comparison of the molecular, physical, and safety characteristics of these three materials. One drawback to BTTN is that it has been reported to be about three times more toxic than NG for rats and about eight times more toxic for dogs.[13]

Despite its excellent properties, BTTN has been unable to compete with the low cost and ready availability of NG, and NG has not yet been replaced in propellant production. 1,2,4-Butanetriol, the precursor for BTTN, is currently being purchased for about $25 per pound. All of the commercial sources are either foreign or depend on foreign made starting materials. As a result, the present cost of BTTN is about $50 per pound, and a truly domestic supply does not exist. By contrast, NG is manufactured from cheap, readily available materials and costs about $1.50 per pound.

In addition, private industry has little interest in manufacturing BT at levels less than a million pounds per year and guaranteeing its suitability for nitration. The BT which was available at the start of this work generally had a purity of about 95 percent, and its contaminants varied in type and level from lot to lot. A consistent and high quality is essential for safe nitration as the process can often be affected drastically by even trace contaminants.

TABLE 1. PHYSICAL PROPERTIES OF 1,2,4-BUTANETRIOL [1,3,4,5]

Structure	$HOCH_2CHOHCH_2CH_2OH$
Empirical Formula	$C_4H_{10}O_3$
Composition	45.3%C, 9.4%H, 45.3% O
Molecular Weight	106
Boiling Point	^oC/mm Hg, 116/0.17, 132/1.5, 179/13
Refractive Index	n_D^{25} 1.473, n_D^{17} 1.4758
Density at 20°	1.184 g/cc
Viscosity at 25°	704cps
with 5% H_2O	380cps
with 10% H_2O	202cps
Flash Point (Cleveland Open Cup)	173^oC
Fire Point (Cleveland Open Cup)	201^oC
ΔH_v	14.0 kcal/mole
ΔH_c	555 kcal/mole

TABLE 2. COMPARISON OF THE MOLECULAR COMPOSITION OF NG, BTTN, AND MTN

	NG	BTTN	MTN
Structure	$CH_2 - ONO_2$ $CH - ONO_2$ $CH_2 - ONO_2$	$CH_2 - ONO_2$ CH_2 $CH - ONO_2$ $CH_2 - ONO_2$	CH_3-C with $CH_2 - ONO_2$ / $CH_2 - ONO_2$ / $CH_2 - ONO_2$

Composition

	NG	BTTN	MTN
%C	15.9	19.9	23.5
H	2.2	2.9	3.5
N	18.5	17.5	16.6
O	63.4	59.7	56.4
M.W.	227	241	255

Oxygen Balance

	NG	BTTN	MTN
CO_2%	3.5	-17	-35
CO%	24.4	10	- 3

TABLE 3. COMPARISON OF PHYSICAL PROPERTIES OF NG, BTTN, AND MTN

	NG	BTTN	MTN
Density: GM/CC 25°C Liquid	1.591	1.52	1.47
Melting Point: °C Labile Form	2.2		
Stable Form	13.2		-3
Boiling Point: °C, Decomposes	145		
Refractive Index, N_D^{25}	1.4732	1.4738	1.4752
Heat of:			
Combustion, cal/gm	1616	2168	2642
Explosion, cal/gm	1600	1457	
Gas Volume, cc/gm	715	840	
Solubility in Water, gm/100 gm, at: 20°C	0.18	0.08	<0.015
Viscosity, Centipoises: Temp, 25°C	29	59	

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TABLE 4. COMPARISON OF SENSITIVITY DATA FOR NG, BTTN, AND MTN

	NG	BTTN	MTN
Impact Sensitivity, 2 kg wt:			
Bureau of Mines Apparatus, cm sample wt 20 mg	15	58	47 (1 lb. wt.)
Picatinny Arsenal Apparatus, in. 1 lb wt sample wt, mg	1	≤1	
Explosion Temperature (5 seconds)	Explodes 222°C	Decomposes 230°C	Ignites 235°C
100°C Heat Test:			
% Loss, 1st 48 hrs	3.6	1.5	2.5
% Loss, 2nd 48 hrs	3.5	1.2	1.8
Explosion in 100 hrs	None	None	None
Vacuum Stability Test: CC/40 hrs, at			
90°C cc/gm/6 hrs	1.6	-	-
100°C cc/gm/16 hrs	11+	2.33	1.9
200 Gram Bomb Sand Test: Sand, gm Liquid Method	51.5	48.6	43.7

The cause of the BT supply problem can be attributed in part to the choice of manufacturing processes which facilitate shifting production from one to another product with a minimum of equipment modification and down time. Since the military demand for BT has been relatively low by industrial standards, it has not been cost effective to optimize reaction conditions, evaluate alternate methods of synthesis, or improve the product purity. As a result, very little effort has been made in this direction.

The main objective of this work was to evaluate methods of synthesis of BT which might be scaled up to a fully domestic second source supply using production equipment already existing at the Naval Ordnance Station, Indian Head (NOSIH). A cost reduction also seemed possible as the cost of potential BT precursors ranged from a few cents to a few dollars per pound.

Since a guaranteed product quality was essential, another objective of the work was to design and demonstrate analytical techniques that could be used on a routine basis to identify and assay trace contaminants in BT. In conjunction with this, it was also desirable to collect data which might eventually permit a correlation between the types and levels of observed impurities with results of nitrations run under conditions simulating those used in the continuous nitration facility at NOSIH.

CHAPTER 2

PREVIOUS SYNTHESIS

Wagner first prepared BT in 1894 by the mild aqueous oxidation of 3-butene-1-ol with potassium permanganate.[14] Since then, more efficient methods

$$CH_2 = CH - CH_2 - CH_2 - OH \xrightarrow[H_2O]{(O)} BT$$
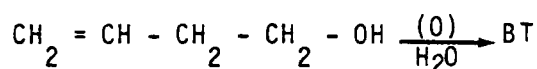
have been developed using either peracids or hydrogen peroxide for the reaction (15 to 23) and Gallaghan et al. reported an 85 percent yield of BT from 3-butene-1-ol using hydrogen peroxide over an osmium tetroxide catalyst.[24] An evaluation of alternate catalysts and conditions has been examined recently at the Naval Surface Weapons Center (NSWC).* The effort also sought to lower the cost of 3-butene-1-ol by modification of the catalytic dehydration method commonly used to produce it from 1,3-butanediol.

$$\underset{\substack{| \\ OH}}{CH_2} - CH_2 - \underset{\substack{| \\ OH}}{CH} - CH_3 \xrightarrow[-H_2O]{CAT., \Delta} \underset{\substack{| \\ OH}}{CH_2} - CH_2 - CH = CH_2$$
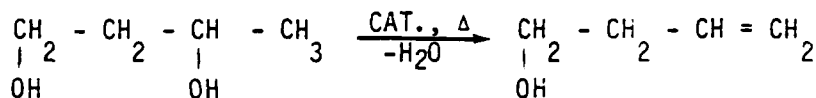
During the second world war, Reppe perfected a method that has been widely used for the commercial manufacture of BT from acetylene and formaldehyde.[25-30]

$$\underset{\substack{||| \\ CH}}{CH} \xrightarrow{CH_2O} \underset{\substack{| \\ CH_2OH}}{\overset{CH_2OH}{\underset{|||}{C}}} \xrightarrow{H_2O/HgSO_4} \underset{\substack{| \\ CH_2OH}}{\overset{CH_2OH}{\underset{|}{\overset{CH_2}{C = O}}}} \xrightarrow{H_2/Ni} BT$$
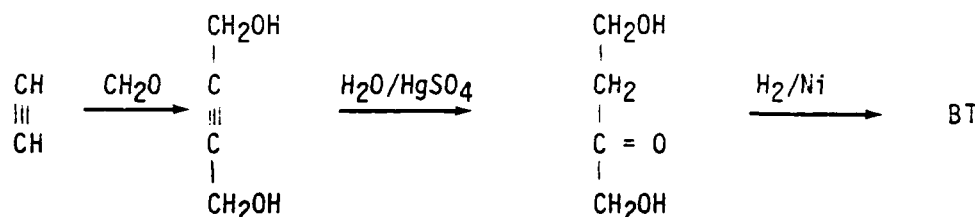
A major disadvantage of the process is the large number of other products concommitently produced through isomerizations and other side reactions. Recent environmental concerns over the use of mercury compounds also cast a shadow over the process.

A new synthesis route to BT was developed in 1948 by the U. S. Rubber Company under a Navy contract.[31,32] A Prins condensation of allyl alcohol or acetate with formaldehyde in a mixture of acetic acid, acetic anhydride, and sulfuric acid yielded 1,2,4-butanetriol triacetate. Subsequent methanolysis of the acetate produced BT.

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*Wagaman, K. L., private communication, 1980.

$$\begin{array}{c} CH_2OH \\ | \\ CH \\ \parallel \\ CH_2 \end{array} \quad \xrightarrow[\text{H}_2\text{SO}_4]{\text{CH}_2\text{O, HOAc}} \quad \left[\begin{array}{c} CH_2OH \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ CH_2OAc \end{array}\right] \quad \xrightarrow{\text{(AcO)}_2\text{O}} \quad \begin{array}{c} CH_2OAc \\ | \\ CH_2 \\ | \\ CHOAc \\ | \\ CH_2OAc \end{array}$$

$$\xrightarrow{\text{CH}_3\text{OH}} \quad BT$$
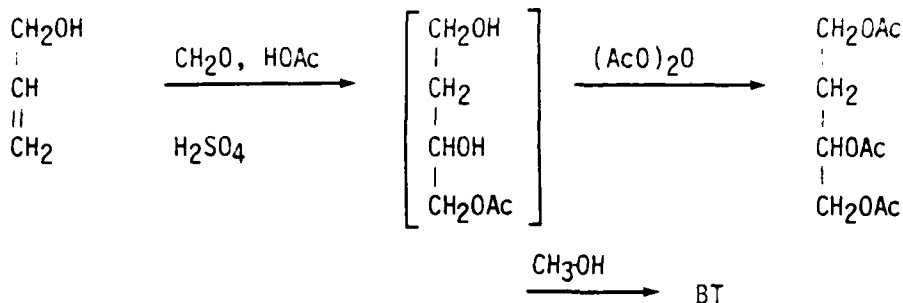
At about the same time, Adkins was evaluating the activity of copper chromite and Raney nickel as hydrogenation catalysts and reported on their use in the reduction of a large number of organic esters.[33,34] One of these, diethyl malate, was converted to BT in 50-60 percent yield, but the synthesis of BT was not an objective of the work and no attempt was made to optimize or scale-up the reaction.

$$\begin{array}{ccc} O & OH & O \\ \parallel & | & \parallel \\ C_2H_5O - C - CH - CH_2 - C - OC_2H_5 \end{array} \quad \xrightarrow{\text{H}_2} \quad BT$$
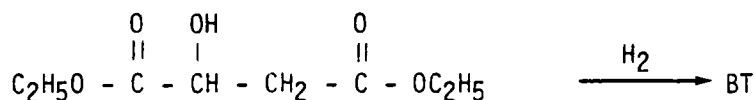
A number of other methods for the preparation of BT or its derivatives have appeared in the literature but either give low yields or depend on commercially unavailable starting materials. Thus, 1-ethoxy-2,4-butanediol was obtained by reduction of the condensation product of ethoxyglycol aldehyde and acetaldehyde.[35] Addition of methanol to 1,4-dimethoxy-2-butyne has been

$$\begin{array}{c} CH_2 - OC_2H_5 \\ | \\ C = O \\ H \end{array} \quad + \quad \begin{array}{c} CH_3 \\ | \\ C = O \\ | \\ H \end{array} \quad \longrightarrow \quad \begin{array}{c} CH_2-OC_2H_5 \\ | \\ CH-OH \\ | \\ CH_2 \\ | \\ C = O \\ H \end{array} \quad \xrightarrow{\text{H}_2} \quad \begin{array}{c} CH_2-OC_2H_5 \\ | \\ CH-OH \\ | \\ CH_2 \\ | \\ CH_2OH \end{array}$$
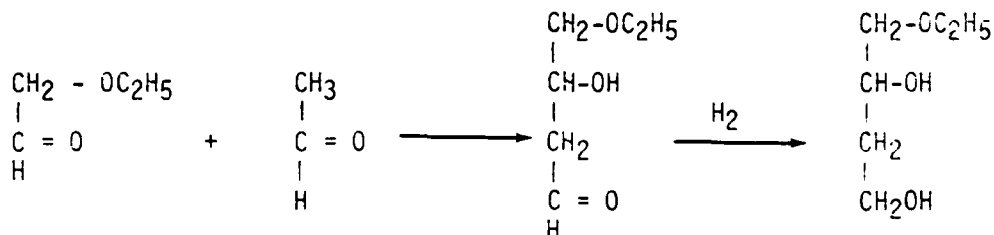
reported to produce 1,2,4-trimethoxy-2-butene, which on reduction yields 1,2,4-trimethoxybutane.[36] Celanese Corporation has a patent for making a

$$\begin{array}{c} CH_2-OCH_3 \\ | \\ C \\ \parallel\!\parallel \\ C \\ | \\ CH_2-OCH_3 \end{array} \quad \xrightarrow[\text{CH}_3\text{ONa}]{\text{CH}_3\text{OH}} \quad \begin{array}{c} CH_2-OCH_3 \\ | \\ C-OCH_3 \\ \parallel \\ CH \\ | \\ CH_2-OCH_3 \end{array} \quad \xrightarrow{\text{H}_2} \quad \begin{array}{c} CH_2-OCH_3 \\ | \\ CH-OCH_3 \\ | \\ CH_2 \\ | \\ CH_2-OCH_3 \end{array}$$
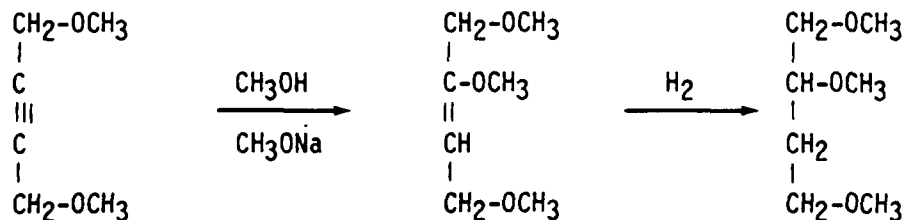
monoepoxide of 1-methoxybutadiene, which on hydrolysis gives 3,4-dihydroxybutanal. This material can then be converted to BT by hydrogenation over Raney nickel.[37]

$$\begin{array}{c} CH_2 \\ \parallel \\ CH \\ \mid \\ CH \\ \parallel \\ CH\text{-}OCH_3 \end{array} \xrightarrow{HO_2AC} \begin{array}{c} CH_2 \\ \mid \\ CH \\ \mid \\ CH \\ \parallel \\ CH\text{-}OCH_3 \end{array} \!\!> 0 \xrightarrow{H_2O} \begin{array}{c} CH_2\text{-}OH \\ \mid \\ CH\text{-}OH \\ \mid \\ CH_2 \\ \mid \\ C = 0 \\ H \end{array} \xrightarrow{H_2/Ni} BT$$
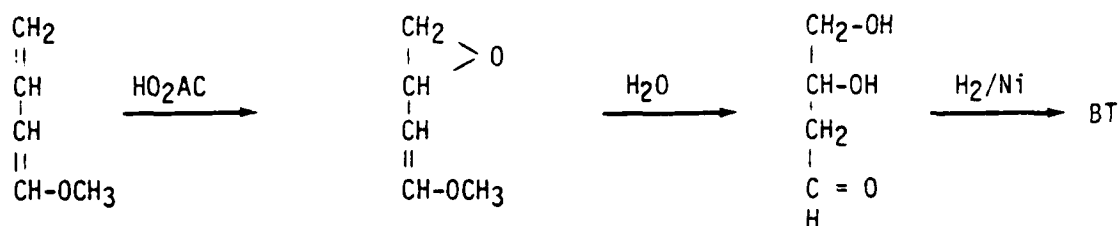
Refluxing of 1,2,4-tribromobutane for long periods with potassium acetate and acetic anhydride has also been reported to produce the triacetate of BT in yields

$$\begin{array}{c} Br \quad Br \quad\quad Br \\ \mid \quad\ \ \mid \quad\quad\ \ \mid \\ CH_2 - CH - CH_2 - CH_2 \end{array} \xrightarrow[(AcO)_2O]{KOAc} \begin{array}{c} OAc \quad OAc \quad\quad OAc \\ \mid \quad\quad \mid \quad\quad\ \ \mid \\ CH_2 - CH - CH_2 - CH_2 \end{array}$$
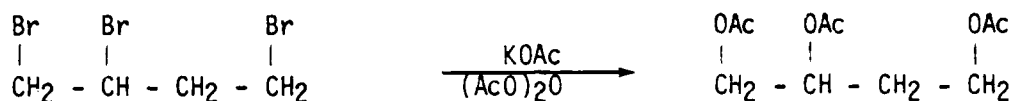
as high as 30 percent,[38] while attempts to hydrate or add acetic acid to 1,4-diacetoxy-2-butene have been unsuccessful.[24]

$$\begin{array}{c} OAc \quad\quad\quad OAc \\ \mid \quad\quad\quad\quad\ \mid \\ CH_2 - CH = CH - CH_2 \end{array} \xrightarrow[(AcO)_2O]{HOAc} \begin{array}{c} OAc \quad OAc \quad\quad OAc \\ \mid \quad\quad \mid \quad\quad\ \ \mid \\ CH_2 - CH - CH_2 - CH \end{array}$$
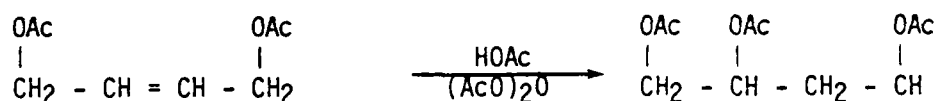
CHAPTER 3

IMPURITY EFFECTS

Because of the diversity of possible contaminants in BT, no one analytical method can be considered completely reliable for the detection or identification of all impurities. Several methods of BT analysis were, therefore, examined so that not only the amount of BT or major impurities in samples could be established, but also so that minor contaminants could be detected and identified. This was considered to be essential since previous work in this laboratory has shown that even trace impurities can drastically affect the nitration process of glycols and the stability of the nitrated product.* The analytical methods examined were infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, gas chromatography (GC), gel permeation chromatography (GPC), and high pressure liquid chromatography (HPLC). In addition, laboratory nitration studies of various lots of BT were initiated to collect data which should eventually permit a correlation between the types and levels of impurities and stability problems encountered during the nitration process. Methods to remove objectionable contaminants were also examined.

SPECTROSCOPIC ANALYSIS

A quantitative IR technqiue has been reported for the analysis of mixtures of 2-butyne-1,4-diol, 2-butene-1,4-diol, and 1,4-butanediol.[39] Since the last two materials are possible contaminants in BT and since similar techniques have been used frequently for polyol analysis, the spectra of a number of lots of BT were examined.

In general the IR and UV spectra of BT samples showed no definitive variations from lot to lot and were judged unsuitable for routine analysis. However, all of the commercially manufactured BT samples examined absorbed light in the 260-265 nm region, which could indicate similar unsaturated impurities. The intensity of the absorption varied from lot to lot suggesting different levels of the unsaturated contaminants.

GC ANALYSIS

Overall, GC was found to be the most rapid, convenient, and useful method for both qualitative and quantitative analysis of BT and related materials. The technique developed in this study has been routinely used for the analysis of both laboratory reaction mixtures and commercially supplied BT.

Tenax was found to be the most effective column packing for obtaining sharp, quick resolution of BT and other high boiling alcohols at a moderate temperature. Columns as long as 2 meters were used, although satisfactory

*Farncomb, R. E. private communications, 1980 through 1981.

resolutions were obtained with a 0.75 meter column. In all cases, nickel column tubing was used as it is more inert than the standard stainless steel tubing and less likely to induce decomposition of reactive organics at elevated temperatures. The columns were usually heated in an oven from 100° to 300°C at 15°C per minute, although other neating rates and temperature ranges were occasionally used to obtain better resolution or quicker results. Likewise, a helium flow rate of 20 ml per minute was generally used but was occasionally varied. On the whole, the length of time that samples were exposed to tne higher tmeperatures was minimized to reduce any thermal decomposition during the analysis. In all of the GC work a hot wire detector was used, and the sample size was generally 0.1 to 1.0 µl. Observed retention times for BT and a number of related compounds under the most commonly used GC conditions are listed in Table 5 and the results of GC analysis of a number of commercially supplied BT samples are summarized in Table 6.

Like most analytical techniques, GC has a number of limitations. First, concentrations are obtained as percent of total peak area, which generally approximates mole percent. Absolute concentration can only be determined when the detector nas been calibrated against an analytically pure standard. Second, nonvolatile materials will not pass through the GC column, and therefore some likely contaminants such as polymers will not be detected. Third, some compounds exhibit essentially identical retention times on the Tenax column and cannot be distinguished. Thus, all of the samples showed one impurity which could have been identified as either 3-hydroxytetrahydrofuran or 1,2-butanediol. Another column packing tnat would resolve these compounds could probably have been found, but the other limitations of GC would still remain. The ambiguity was surmounted by GPC analysis, discussed below, which indicated an absence of both 1,2- and 1,3-butanediol. The presence of some 1,3-butanediol in most of the samples had been indicated by GC data.

GPC ANALYSIS*

To complement the GC analysis, a GPC method for BT analysis was also developed. Since the technique separates components based on their molecular size, compounds such as 3-hydroxytetrahydrofuran an 1,2-butanediol can easily be distinguished while compounds having a similar molecular size, such as 1,2- and 1,3-butanediol cannot be resolved. Furthermore, since the sample is dissolved in a solvent while being partitioned, many nonvolatile materials, such as polymers, can be analyzed. It should be readily apparent that a comparison of analytical data from at least two independent techniques, such as GC and GPC, is imperative to reliably detect, identify, and assay the contaminants in BT samples.

In the GPC method developed, both a refractive index (RI) and a 254 nm UV detector were used. A comparison of the responses of these provided information on both the quantity and nature of components of a mixture. The RI detector responds almost linearly to concentrations, and trace amounts of materials may not be detected. The UV detector responds to absorbance of radiation at 254 nm and is highly sensitive to even trace quantities of compounds containing chromophoric groups such as carbonyls. Materials, such as saturated alcohols, that do not absorb radiation at 254 nm cannot be detected.

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*Richardson, A. C., private communication, Jun 1980.

TABLE 5. GC RETENTION TIMES FOR BT AND RELATED COMPOUNDS USING A 1M TENAX PACKED NICKEL COLUMN HEATED FROM 100-300°C AT 15°C/MIN WITH A HELIUM FLOW OF 20 ML/MIN

Compound	Retention Time (min)*
Water	0.45
Ethanol	1.15
2-Butanol	3.05
3-Butene-1-ol	3.10
Tetrahydrofuran	3.15
1-Butanol	3.60
2,3-Butanediol	5.30
1-Butene-3,4-diol	5.80
1,2-Butanediol	5.85
3-Hydroxytetrahydrofuran	5.85
1,3-Butanediol	6.20
1,4-Butanediol	6.90
2-Butene-1,4-diol	7.15
2-Butanone-1-hydroxyacetate	7.20
1,2,4-Butanetriol	8.90
Dimethylmalate	8.90
Diethylmalate	9.50
2-Butene-1-ol	9.80

*Average retention time is rounded to nearest 0.05 min.

TABLE 6. GAS CHROMATOGRAPHIC ANALYSIS OF 1,2,4-BUTANETRIOL SAMPLES (% OF TOTAL PEAK AREA, EXCLUDING THE PEAK FOR WATER)

Sample Source	1,2,4-Butanetriol (%)	2-Butene-1,4-diol (%)	1,4-Butanediol (%)	3-Hydroxytetrahydrofuran (%)	No. of Other Peaks >0.5%	No. of Other Peaks <0.5%
BASF-583-0770	96.0	0.1	0	1.8	2	0
BASF-583-0771	93.9	0.2	0	1.0	3	3
Eastman	94.0	0	2.1	2.3	2	2
Chem. Sam. Co. Z-3690	98.0	0.3	0	0.5	1	1
Chem. Sam. Co. Lot 24071GA	93.4	1.7	0	1.6	3	2
GAF Lot 35 (1955)	96.6	0.5	0	1.5	2	0
GAF Cut 13 LS-4259G-5538 (1948)	97.8	0.3	0	0.8	2	1
Press. Chem. Lot 1	92.4	0	3.8	3.1	0	4
GAF Cut 13 after carbon treatment	95.1	1.1	0	1.9	3	1
Press. Chem. Lot 1 after carbon treatment	90.1	0	3.9	3.5	2	2

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Gel permeation chromatography was run using five high molecular weight columns, 10^6 and 10^2A microstyragel, and stabilized tetrahydrofuran solvent. All of the BT samples showed evidence of a number of impurities; however, the peaks were inadequately resolved for a practical analysis. A set of low molecular weight columns, two 100A and two 40A microstyragel, gave very good peak resolutions and was used for all subsequent work.

Where possible, peaks were identified by comparing their elution volume with those of known substances. Table 7 lists elution volumes for BT and some related compounds and is reproducible to within 0.1 ml under the conditions used. Since analytically pure standards were not available to calibrate response factors for each material, the concentration of each major component was estimated by dividing the height of each peak indicated by the RI detector by the sum of the samples RI peak heights. All of the samples showed a number of UV active trace impurities as indicated by the 254 nm detector. Table 8 summarizes the analytical results.

HPLC ANALYSIS*

An HPLC method was also demonstrated for the analysis of impurities in BT. A radial packed "A" column was used with water as the carrier solvent, and the effluent was monitored by an RI detector. A flow rate of 1 ml per minute was found to be satisfactory. While good response was obtained with a sample size of 0.02 mg for essentially pure compounds, samples of 45-65 mg of BT were required to adequately detect minor impurities. Retention times and detector response are listed in Table 9 for BT and several related compounds, and the results of an HPLC analysis of the impurities found in BT samples are summarized in Table 10. A comparison of the results of GC, GPC, and HPLC analysis of BT samples is given in Table 11.

NITRATION STUDIES**

Based on previous work in this laboratory,** trial nitrations that simulate actual conditions in the continuous nitration facility at NOSIH were run on commercially supplied BT. Standard potassium iodide (KI) tests were obtained to determine the stability of the nitrated product. Data are summarized in Table 12.

Following a procedure developed by Gelardo and Reitlinger for increasing the stability of nitrate esters,[40] BTTN having only a 4 to 5 minute KI test (from Chem. Sanco BT Lot #3) was washed with aqueous $NaBH_4$ and then thoroughly with water. The resulting BTTN gave a satisfactory 24-minute test. The minimum acceptable value is 10 minutes.

*Carlson, D., private communication, Jul 1980.
**Farncomb, R. E., private communication, 1980 through 1981.

TABLE 7. GPC ELUTION VOLUMES FROM LOW M.W. COLUMNS FOR BT AND SOME RELATED COMPOUNDS

Compound	Elution Volume (ml)
Malic Acid	34.9
1,2,4-Butanetriol	36.7
1,4-Butanediol	38.2
2-Butene-1,4-diol	38.4
1,2-Butanediol	38.7
1,3-Butanediol	38.7
3-Hydroxytetrahydrofuran	42.6

TABLE 8. GEL PERMEATION CHROMATOGRAPHY OF 1,2,4-BUTANETRIOL SAMPLES USING LOW MOLECULAR WEIGHT COLUMNS

Sample Source	Major Components Shown by Refractive Index Detector					Additional Trace Compounds Shown by 254 nm UV Detector[a]
	1,2,4-Butanetriol (%)	2-Butene-1,4-diol (%)	1,4-Butanediol (%)	3-Hydroxytetrahydrofuran (%)	No. of Others	
BASF-583-0770	89.7	1.1	0	0.6	4[b]	9
BASF-583-0771	89.0	2.8	0	0.6	5[c]	9
Eastman	91.4	0	1.5	0	5	7
Chem. Sam. Co. Z-3690	93.9	0	0	1.6	4[d]	5[f]
Chem. Sam. Co. Lot 24071-GA	93.7	0	0	1.6	2	6
GAF Lot 35 (1955)	94.0	0	0	1.6	4	4
GAF Cut 13 LS-4259 G-5538 (1948)	94.9	0	0	0.7	4	3
Press. Chem. Lot 1	87.3	0	3.3	2.3	5[e]	10
GAF Cut 13 After Carbon Treatment	89.1	J	0	4.9	2	5
Press. Chem. Lot 1 After Carbon Treatment	78.7	0	1.5	18.7	1	7

[a] Still other trace compounds may be present and undetected if they are not UV active at 254 nm.
[b] One of these, having an elution volume of 36.0 ml and a concentration of 6.0%, is also UV active at 254 nm.
[c] One of these, having an elution volume of 36.0 ml and a concentration of 5.2%, is also UV active at 254 nm.
[d] One of these, having an elution volume of 35.0 ml and a concentration of 1.9%, is also UV active at 254 nm.
[e] One of these, having an elution volume of 32.0 and a concentration of 0.5%, is also UV active at 254 nm.
[f] Data obtained with the UV detector indicates one of these components to be malic acid.

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TABLE 9. RETENTION TIMES AND DETECTOR RESPONSE FOR HPLC ANALYSIS OF BT AND SOME RELATED COMPOUNDS

Compound	Retention Time (min)	Peak Height (mm) for a 0.02mg Sample
1,2,4-Butanetriol	4.4	-
2-Butene-1,4-Diol	7.30	52
1,3-Butanediol	9.50	29
1,4-Butanediol	10.82	41

TABLE 10. HEIGHT (mm) OF IMPURITY PEAKS OBTAINED FROM HPLC ANALYSIS OF 45-65 mg SAMPLES OF BT

Sample	Retention Time, min							Total Height of Impurity Peaks (mm)
	3.28	3.90	5.02	6.46	7-8	9.82	10.50	
"BT from Pressure Chem"	2	2	-	-	-	24	24	52
"BT 90% BASF 6830187"	10	-	-	-	-	-	2	12
"BT 94% BASF 6830188"	10	-	-	-	2	-	2	14
"BT 96% BASF 5830770"	101	-	(sh)	-	-	-	10	111 + (sh)
"BT 94% BASF 5830771"	101	-	(sh)-22	-	-	2	10	133
"BT cut 35 GAF"	4	2	-	-	-	-	5	11
"BT Chem. Sam. Co. Sample #2"	6	13	(sh)	3	-	-	5	27 + (sh)
"BT Pressure Chem. Carbon Treated"	2	-	-	-	-	23	22	47
"BT GAF Carbon Treated"	2	-	-	-	2	-	3	7
"BT Eastman"	3	-	-	-	-	14	4	21
"BT Chem. Sam. Co. Sample #1"	3	4	-	1	-	-	-	8
"BT Sam. Co. #3"	3	4	2	-	-	-	-	8

(sh) = shoulder on BT peak

TABLE 11. COMPARISON OF BT ANALYSIS BY GC, GPC, AND HPLC

Sample Source	% 1,2,4-Butanetriol		Number of Major Impurities Detected		
	By GC	By GPC	By GC	By GPC	By HPLC
BASF-583-0770	96.0	89.7	4	6	3
BASF-583-0771	93.9	89.0	8	7	4
Eastman	94.0	91.4	6	6	3
Chem. Sam. Co. Z-3690	98.0	93.9	4	5	3
Chem. Sam. Co. Lot 24071GA	93.4	93.7	7	3	7
GAF Lot 35 (1955)	96.6	94.0	6	5	3
GAF Cut 13 LS-4259G-538 (1948)	97.8	94.9	5	5	-
Press. Chem. Lot 1	92.4	87.3	6	7	4

TABLE 12. KI STABILITY OF BTTN FROM TRIAL NITRATION OF VARIOUS LOTS OF BT

BT Source and Treatment of BTTN	BTTN KI, Test Time, Min
94% BASF BT 6830188 2nd 19%	22
Chem. Sanco #3 NaNH$_4$ treatment	24
Chem. Sanco #3	5
Chem. Sanco #3 from H$_2$O emulsion	4
Lot #9	25
GAF Lot #13	25 +
Chem. sanco	4
94% BASF 5830771	27
90% BASF BT	8
96% BASF	20 +
90% BASF Same as above	8
10% 3-HTHF added to GAF Lot #13	8
Treated with NaBH$_4$, 96% BASF	23
Chem. sanco #2	13
Chem. sanco #1	25
Chem. sanco #1 NaCO$_3$ wash overnight	20 +
Chem. sanco #1 NaCO$_3$ plus NaBH$_4$ wash	15 +
Specifications	>10

One of the impurities commonly found in BT that has been postulated to cause problems is 3-hydroxytetrahydrofuran (3-HTHF). The compound can be formed by dehydration of BT during distillation. Addition of ten percent 3-HTHF to GAF lot #13 lowered the KI stability of the nitration product from 25 to 3 minutes.

REMOVAL OF IMPURITIES

To remove some of the contaminants in BT, samples were passed through a column of freshly activated Filtasorb 400 granulated carbon. Initially dark yellow, very viscous BT was converted to colorless, less viscous material. Gas chromatographic analysis indicated only slight changes after the carbon treatment; however, GPC and HPLC showed that significant changes in the concentrations of impurities had occurred (Tables 6, 8, and 10). Some contaminants had either been completely or partially removed; however, the level of 3-HTHF appeared to increase. This is assumed to be a result of using thoroughly dried carbon which absorbs water exothermically and could have promoted the ring-closing dehydration of BT. In all subsequent work, the BT was dissolved in water and passed through wet carbon.

In an alternate purification technique, odorous substances have been reported to be removed from glycols by treating them with a metal hydride, followed by addition of water and distillation.[41] This technique may be applicable to the removal of some of the impurities found in commercial BT, but it has not yet been thoroughly examined.
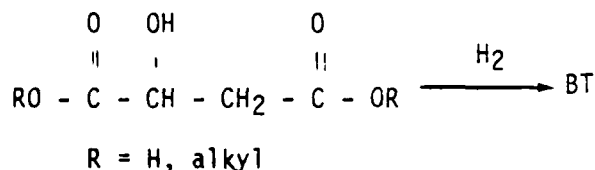
CHAPTER 4

SYNTHESIS

HYDROGENATION OF MALIC ACID AND ITS ESTERS

1,2,4-Butanetriol possesses an asymmetric carbon atom, carbon number two, and can exist as optical isomers. Nitration of a racemic mixture or optically active material would produce the corresponding racemic or optically active BTTN. These materials should have different freezing point characteristics, and a comparison of their performance in propellants would be of interest.

Perhaps the only available method to selectively obtain either racemic or optically active BT is the reduction of malic acid or its derivatives. Table 13 lists the optical rotations, melting points, and boiling points of malic acid and several esters.[42] Laboratory scale synthesis could be performed conveniently with such reagents as lithium aluminum hydride[43] or borane-methyl sulfide;[44] however, on a larger scale, these reagents would probably be too hazardous and expensive for practical application.

By contrast, direct catalytic hydrogenation of organic acids and esters is a routine production process. Its application to malic acid could provide not only a route to optically active BT, but also a very low cost synthesis. Based on

$$
\underset{\text{R = H, alkyl}}{RO - \overset{\overset{\text{O}}{\|}}{C} - \overset{\overset{\text{OH}}{|}}{CH} - CH_2 - \overset{\overset{\text{O}}{\|}}{C} - OR} \xrightarrow{\text{H}_2} BT
$$

a price of \$0.65 per pound for commercial quantities of malic acid and only a 50 percent conversion, the cost of chemicals to produce one pound of BT would be about \$1.50 or \$3.50 if the principal starting material were malic acid or diethylmalate, respectively.

Experiments were designed to evaluate and compare the effectiveness of a number of catalysts, solvents, and reaction conditions. In general, a one liter stirred autoclave was first charged with the malic acid or ester, solvent, and catalyst. It was then sealed, purged several times with nitrogen, pressurized with hydrogen, and finally heated. Because of the limitations of the production equipment that would be available for scale-up, the maximum pressure was kept below 3000 psi. The reaction was monitored both by the pressure drop and by periodically withdrawing small samples for gas chromatographic analysis. Figures 1 through 9 show some of the pressure/time curves that were obtained.

TABLE 13. OPTICAL AND PHYSICAL PROPERTIES OF MALIC ACID AND ITS ESTERS

Compound	$(\alpha)_D^{20}$	m.p. (°C)	b.p. (°C)
D,L-Malic Acid	-	133°	-
L(-)-Malic Acid	5.9° (acetone)	100°	-
D-Malic Acid	-5.9°	98-9°	-
Dimethyl-D,L-malate	-	-	242°
Dimethyl-L-malate	-6.9°	-	122°/12mm
Diethyl D,L-malate	-	-	255°
Diethyl L-malate	-10.2°	-	129°/12mm
Di-n-Propyl L-malate	-11.6°	-	150°/12mm
Di-n-butyl L-malate	-10.7°	-	170°/12mm

FIGURE 1. HYDROGENATION OF DIETHYLMALATE IN ETHANOL OVER NIKKI 203-SD COPPER CHROMITE AT 150°C
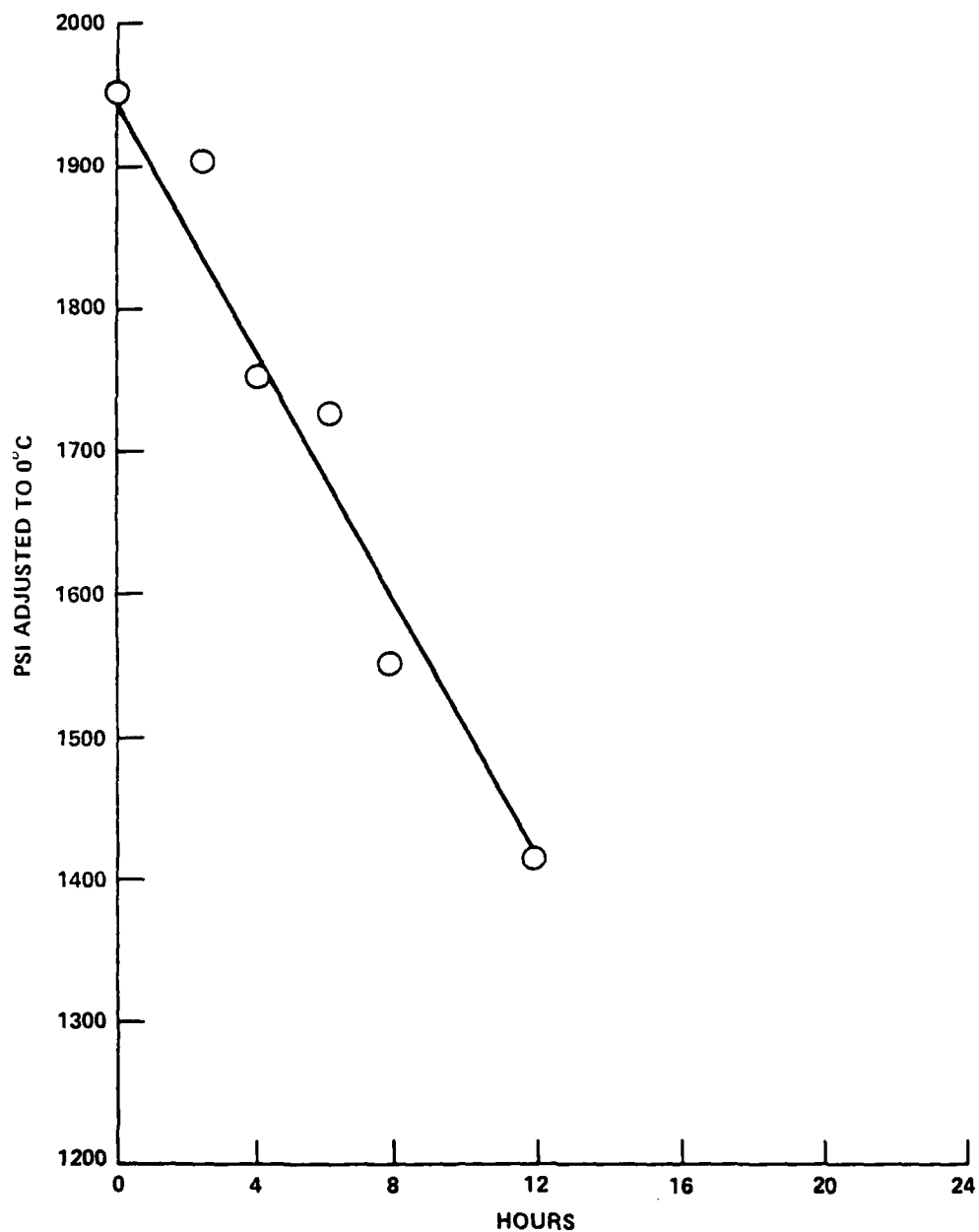
FIGURE 2. HYDROGENATION OF DIETHYLMALATE OVER NIKKI 203-SD COPPER CHROMITE AT 62°C WITHOUT SOLVENT

FIGURE 3. HYDROGENATION OF DIETHYLMALATE OVER NIKKI 203-SD COPPER CHROMITE AT 112°C WITHOUT SOLVENT

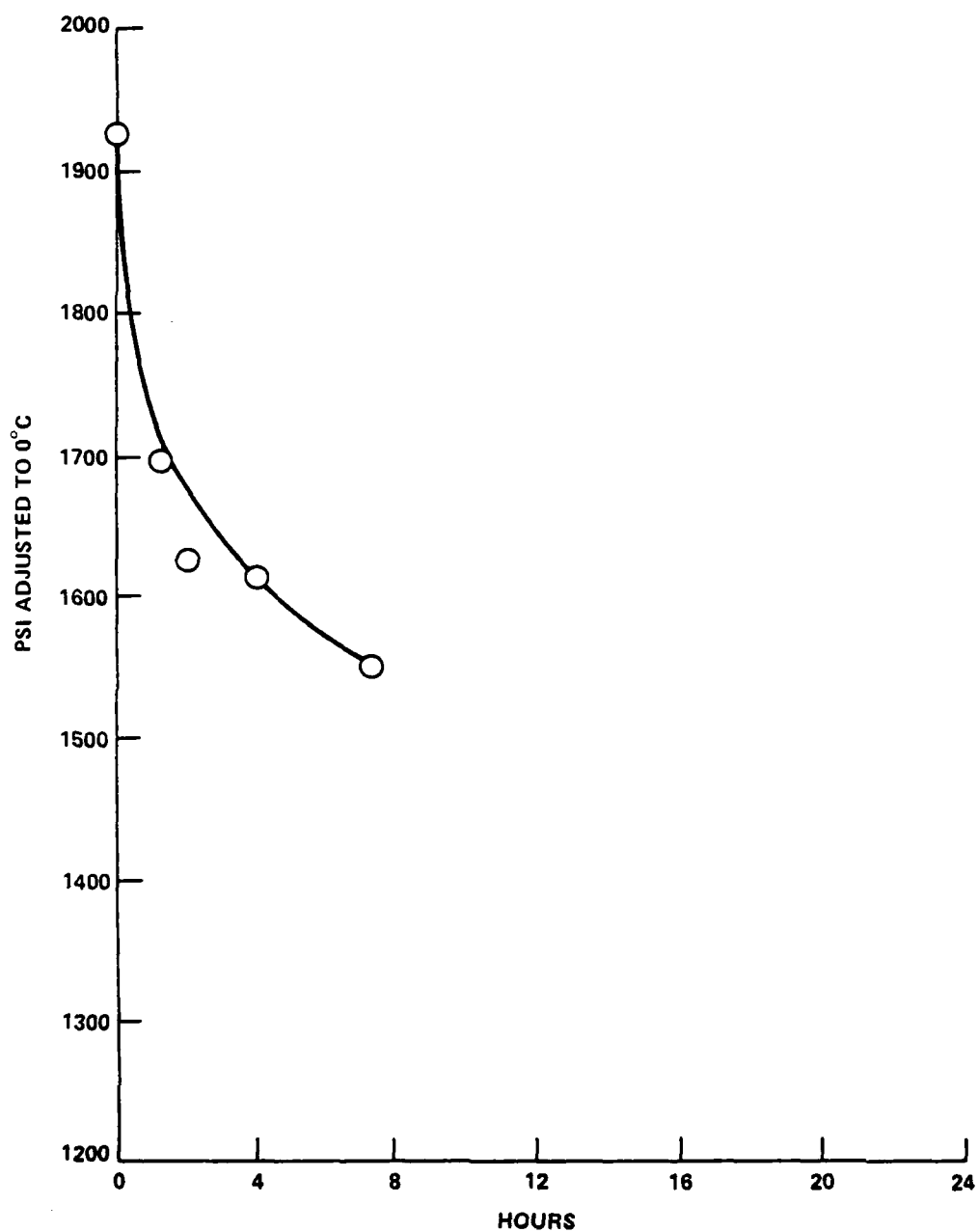FIGURE 4. HYDROGENATION OF DIETHYLMALATE OVER NIKKI 203-SD COPPER CHROMITE AT 150°C WITHOUT SOLVENT

FIGURE 5. HYDROGENATION OF DIETHYLMALATE IN ETHANOL OVER NIKKI 203-SD COPPER CHROMITE AT 108°C

FIGURE 6. HYDROGENATION OF DIETHYLMALATE IN 50% AQUEOUS ETHANOL OVER NIKKI 203-SD COPPER CHROMITE AT 155-160°C

FIGURE 7. HYDROGENATION OF DIETHYLMALATE OVER NIKKI 203-SD COPPER CHROMITE AT 125°C WITH A LITTLE TRIETHYLAMINE ADDED
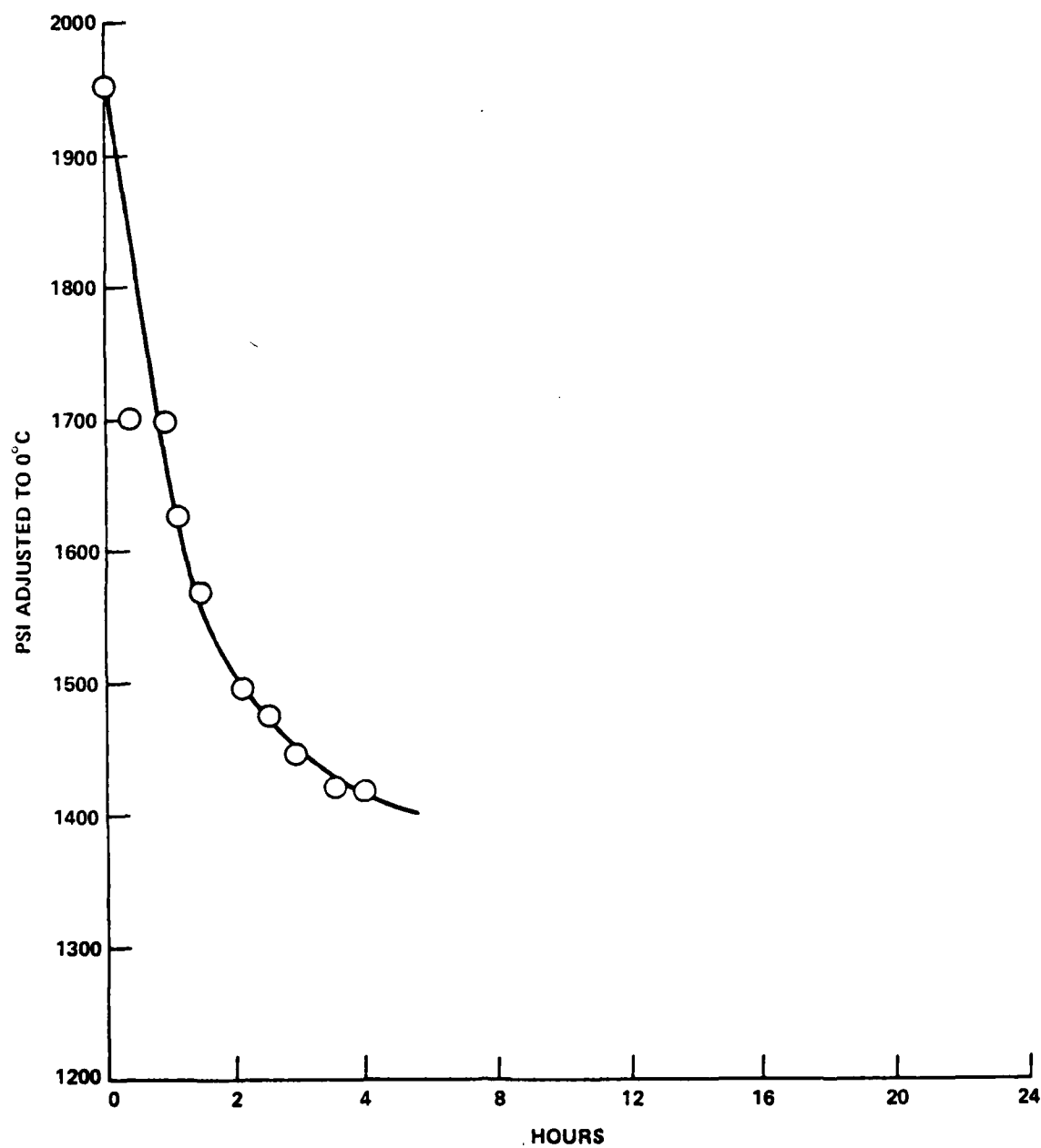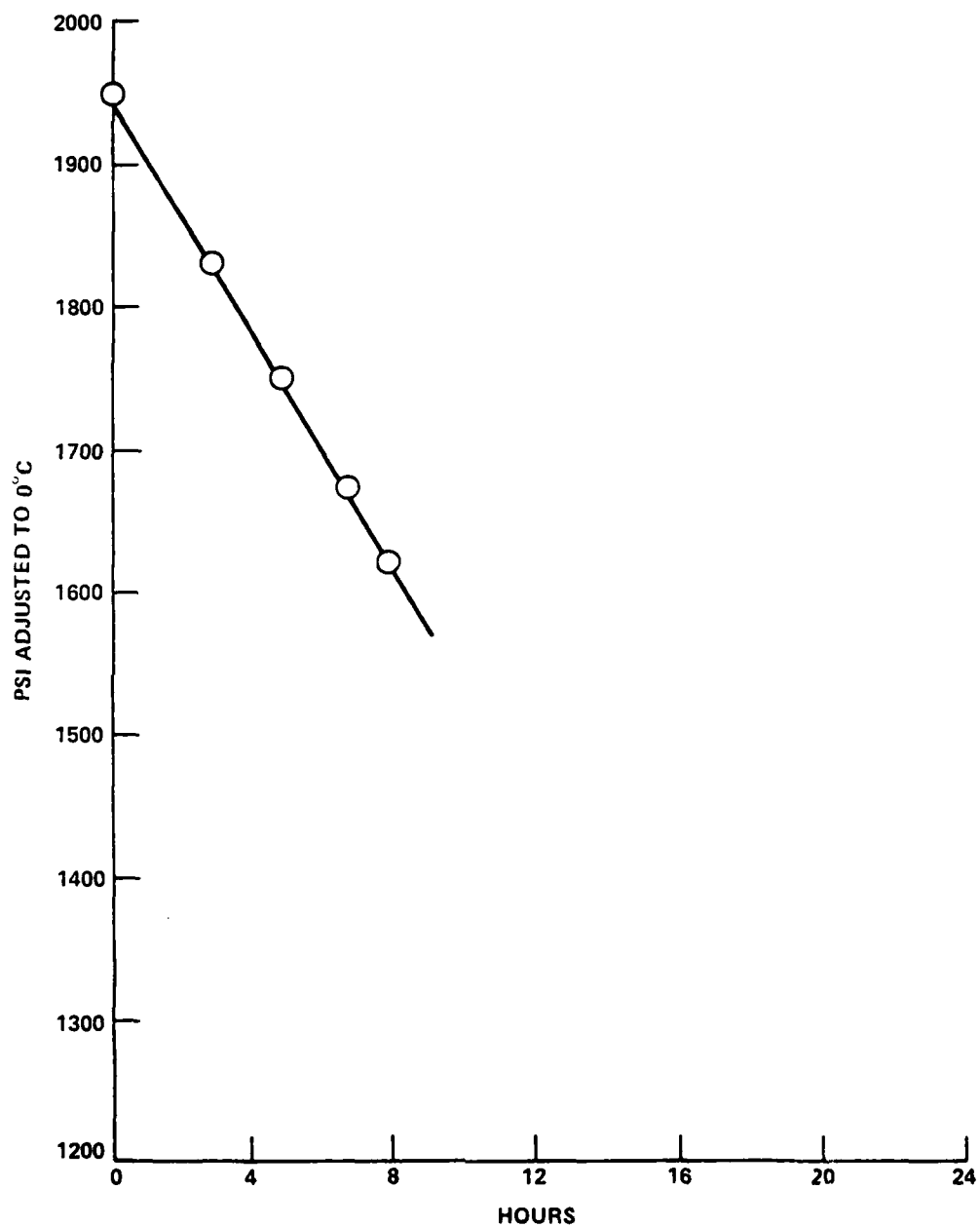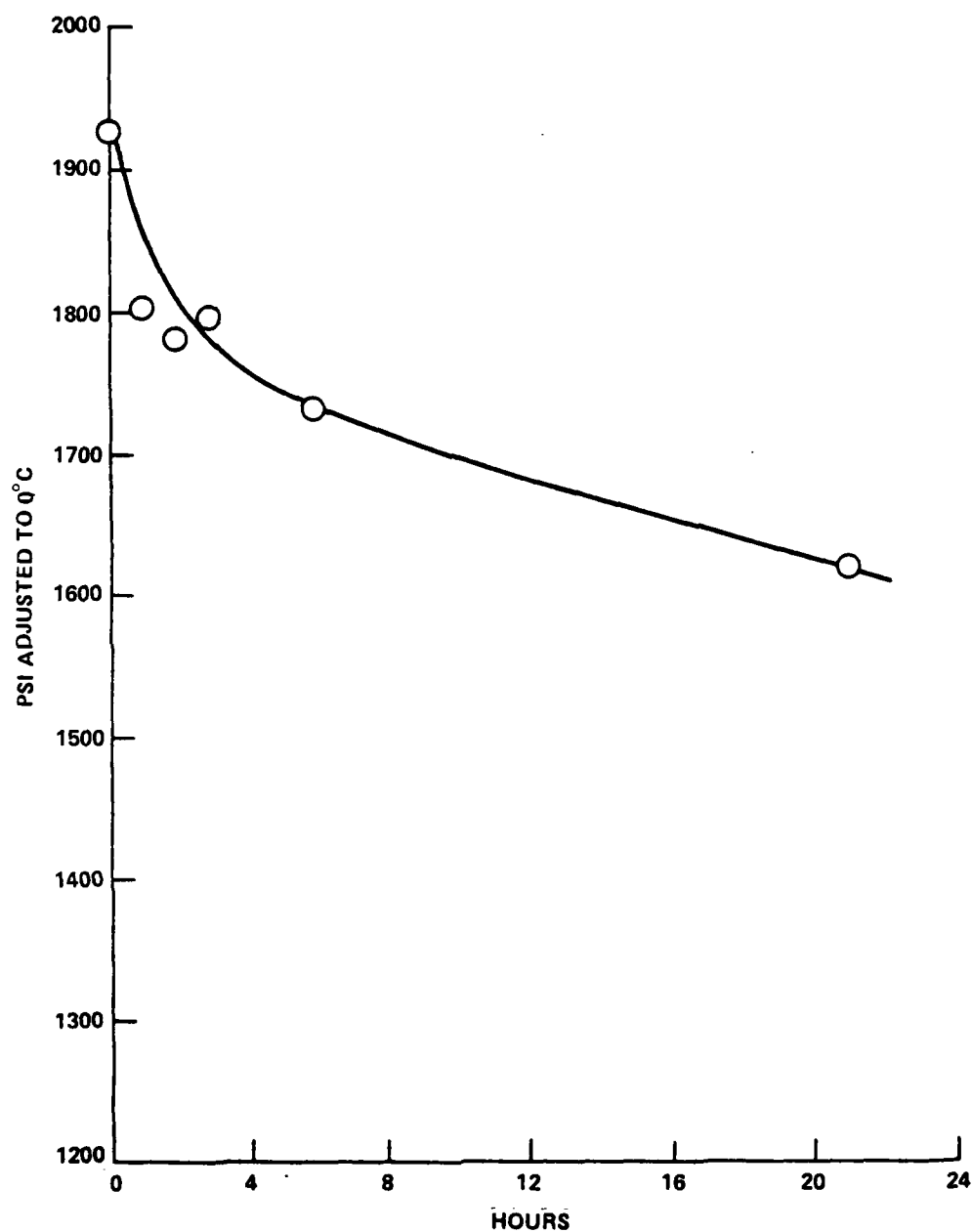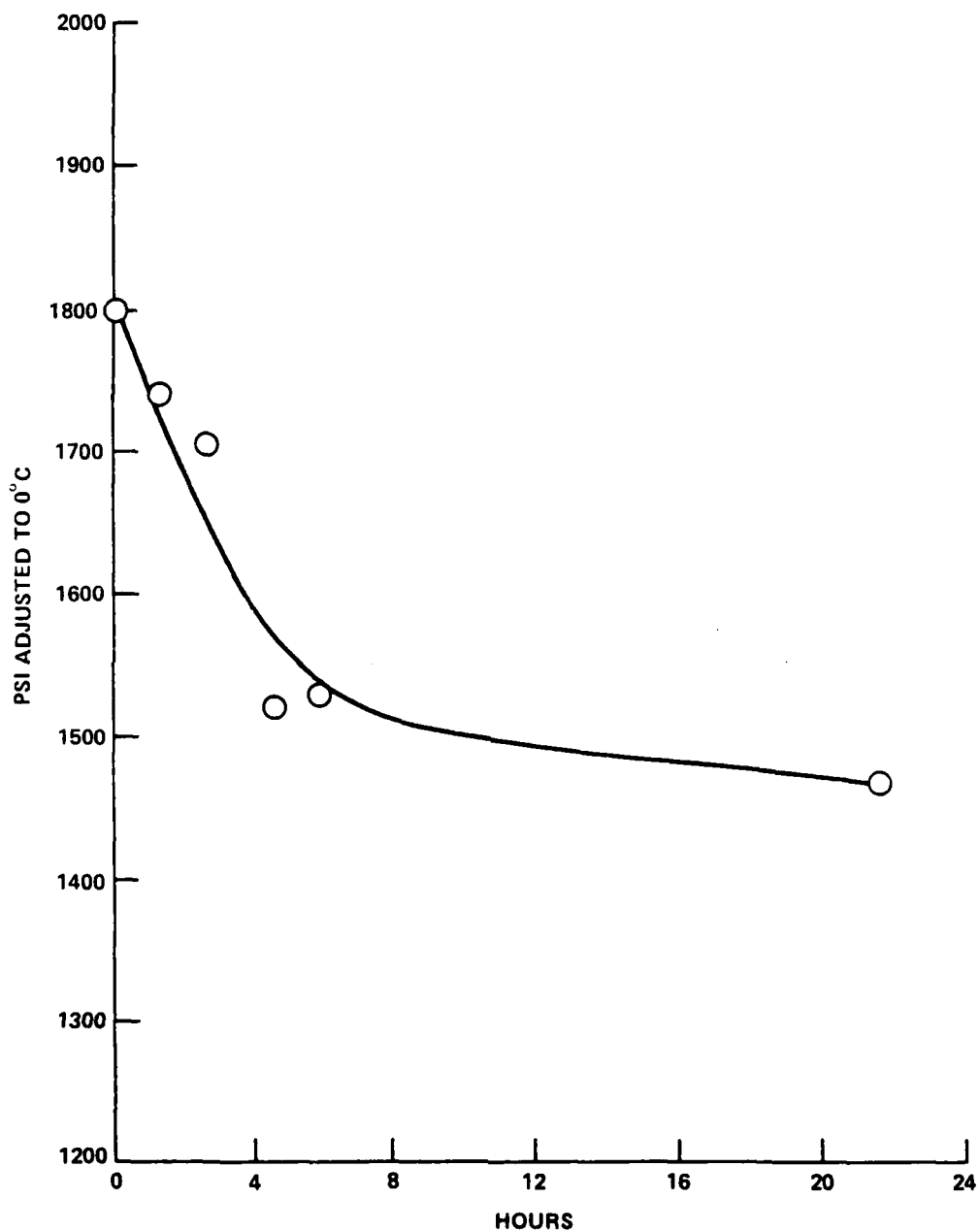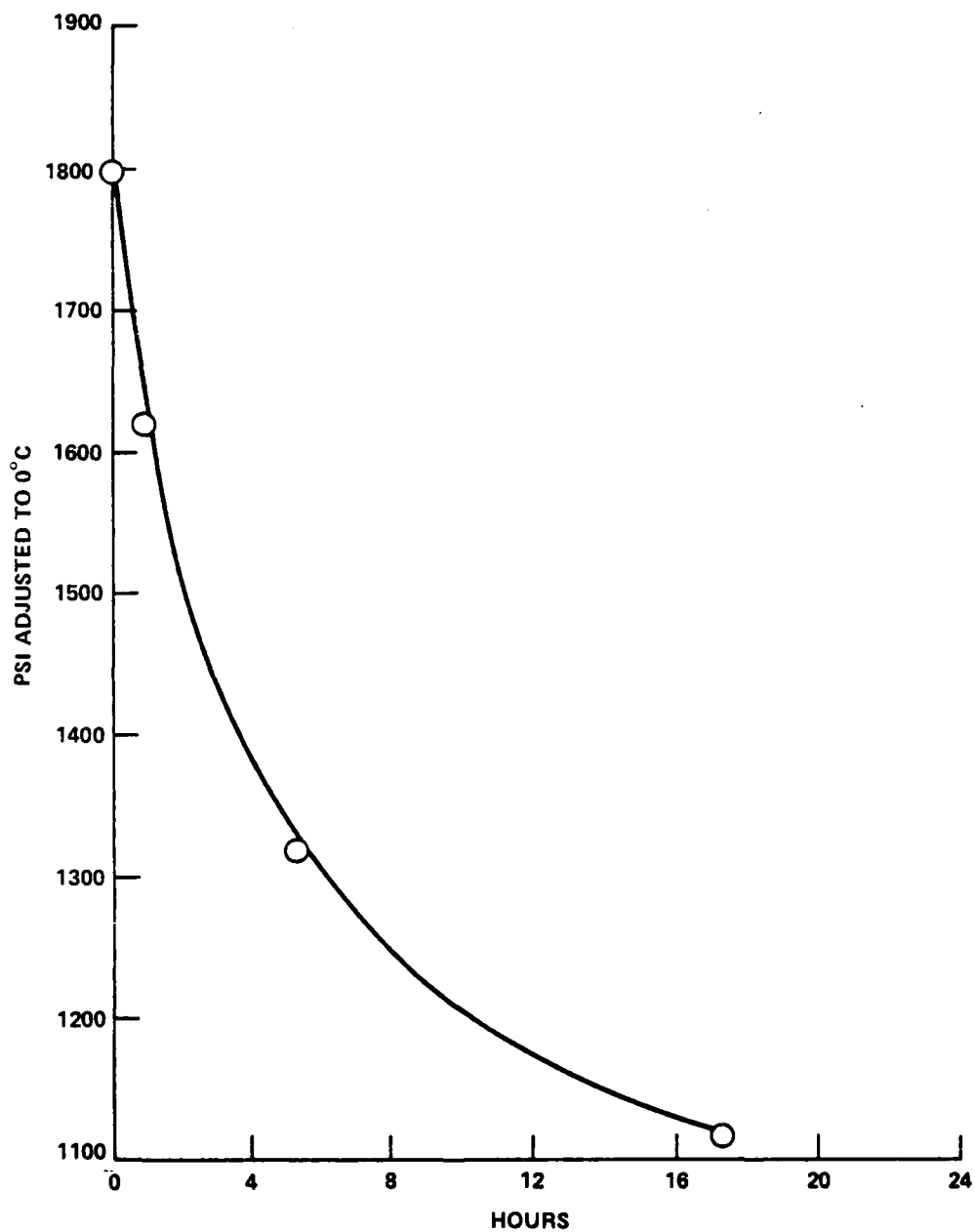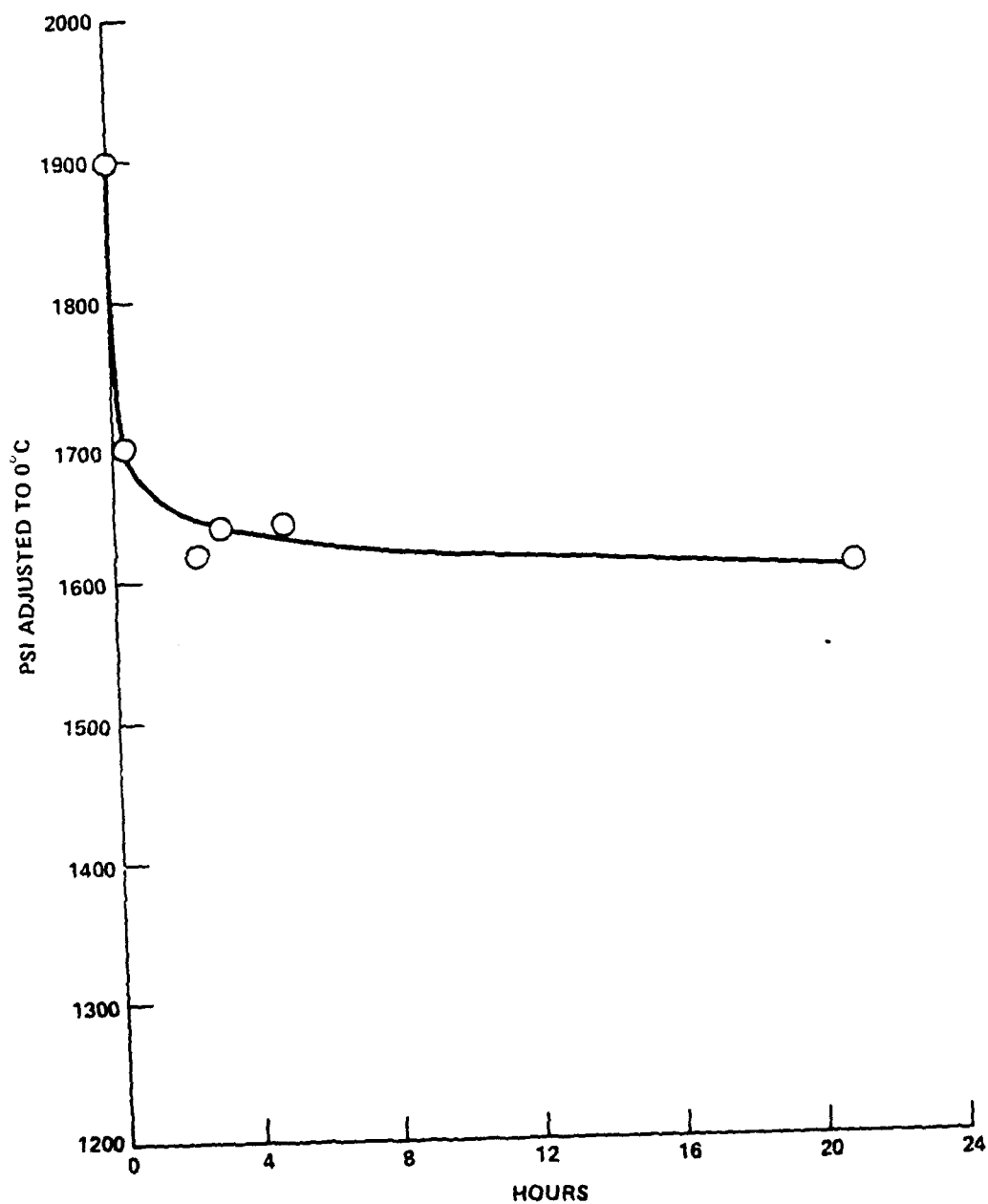
FIGURE 8. HYDROGENATION OF DIETHYLMALATE OVER RANEY NICKEL-28 WITH 1% TRIETHYLAMINE AT 130°C
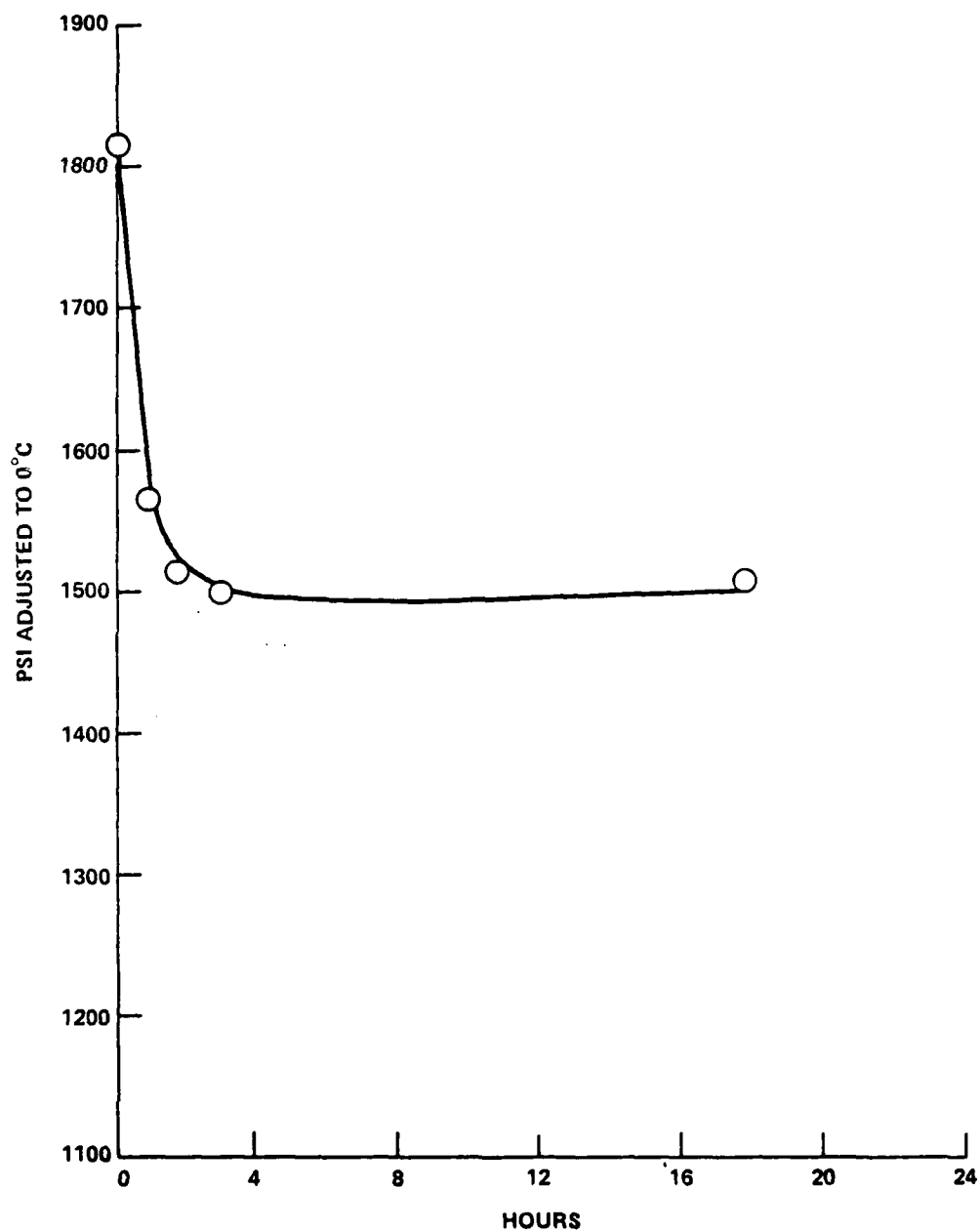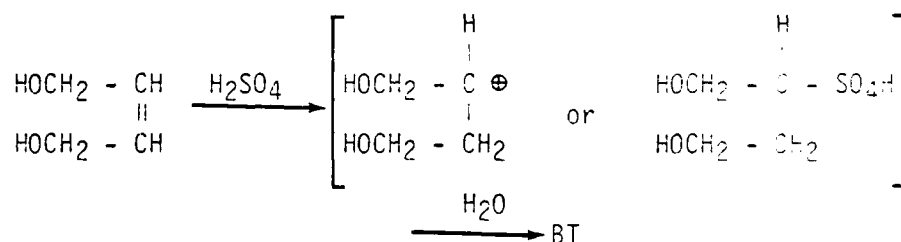
FIGURE 9. HYDROGENATION OF DIETHYLMALATE OVER RANEY NICKEL-20 WITH 12% TRIETHYLAMINE AT 125°C

For the reduction of malic acid, W. R. Grace & Co's Raney 28 and Raney 200 nickel catalysts were used with water or 60, 70, 80, and 90 percent aqueous ethanol at initial pHs of 7 to 12 and an initial hydrogen pressure of 1500 psi and temperatures of 80° through 150°C. Nikki's 203-SD copper chromite and Girdler's G-66-BRS copper-zinc catalysts were also tried in ethanol at 1500 psi and temperatures ranging up to 150°C for periods of up to 48 hours. In all cases insignificant yields of BT were obtained.
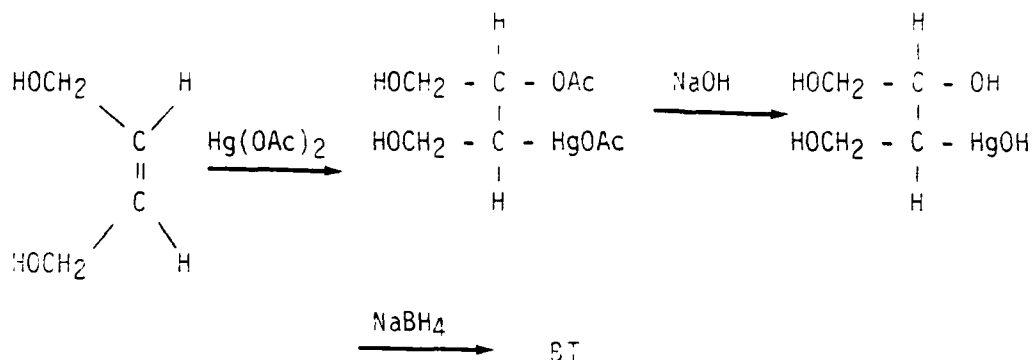
Reduction of diethyl malate was more successful. A number of catalysts were examined, and copper chromite was found to give the best combination of yield and limited side-products. A 30 percent conversion to BT and a very small amount of 1,4-butanediol were obtained in ethanol solution over Nikki's 203-SD copper chromite. Conversions of about 10 percent were obtained over ruthenium or a mixture of ruthenium and palladium on carbon, while palladium or platinum on carbon produced lower yields. In all of these reactions water, ethanol, 50 percent aqueous ethanol, and excess diethyl malate were examined as solvents. Water gave the poorest results, while ethanol or excess diethyl malate appeared equally effective, and the addition of a small amount of triethylamine appeared to accelerate the reaction rate. Complex mixtures of products containing BT in yields of up to 20 percent were obtained over W. R. Grace's Raney nickel 28 and Raney nickel 200 in 60 to 90 percent aqueous ethanol at initial phs of 8 to 12. In all of the above reactions, the hydrogen pressure was 2000 to 3000 psi, the temperature was varied up to 150°C, and the contact time was up to 24 hours. The results suggested that a reasonable production rate might not be achieved at pressures below 2500 psi, which is above the limit of the production equipment presently available at NOSIH.

ACID CATALYZED HYDRATION OF 2-BUTENE-1,4-DIOL

$$
\begin{array}{c}
\mathrm{HOCH_2 - CH} \\
\| \\
\mathrm{HOCH_2 - CH}
\end{array}
\xrightarrow{\mathrm{H_2SO_4}}
\left[
\begin{array}{ccc}
& \overset{\textstyle H}{\underset{\textstyle |}{\mathrm{HOCH_2 - C \oplus}}} & \overset{\textstyle H}{\mathrm{HOCH_2 - C - SO_4H}} \\
& \underset{\textstyle |}{\mathrm{HOCH_2 - CH_2}} \quad or & \mathrm{HOCH_2 - CH_2}
\end{array}
\right]
$$

$$\xrightarrow{\mathrm{H_2O}} \mathrm{BT}$$

2-Butene-1,4-diol is readily available at a cost of about $1.50 per pound and its physical and physiological properties are well established.[45] Its acid catalyzed hydration would probably offer the cheapest way to prepare BT if suitable reaction conditions were found. However, while hydrations of this type are applicable to a variety of olefins[46,47] including hydroxy-olefins such as methallyl alcohol, $CH_2 = C(CH_3)CH_2OH$,[48] the free hydroxyl groups of 2-butene-1,4-diol cause a predominant formation of polymeric and cyclic condensation products. Thus, aqueous solutions containing ten percent of the olefin and one to six percent of sulfuric acid at room temperature slowly produced a little BT in a complex mixture of products. Refluxing or treatment with more concentrated acid rapidly produced complex mixtures, tar, and no discernable BT. Reactions run in acidic solutions of sodium bisulfate or potassium sulfate gave similar results.

HYDRATION OF 2-BUTENE-1,4-DIOL VIA OXYMERCURATION-DEMERCURATION

$$HOCH_2 \quad H \quad \underset{C}{\overset{\underset{\displaystyle C}{\parallel}}{\big/}}\!\!\! \underset{HOCH_2}{\big/}\!\!\! \overset{H}{\big\backslash} \quad \xrightarrow{Hg(OAc)_2} \quad \begin{array}{c} HOCH_2 - \overset{H}{\underset{\displaystyle HgOAc}{\underset{\displaystyle |}{\overset{|}{C}}}} - OAc \\ HOCH_2 - C - HgOAc \\ H \end{array} \quad \xrightarrow{NaOH} \quad \begin{array}{c} HOCH_2 - \overset{H}{\underset{\displaystyle H}{\underset{\displaystyle |}{\overset{|}{C}}}} - OH \\ HOCH_2 - C - HgOH \\ H \end{array}$$

$$\xrightarrow{NaBH_4} \quad BT$$

2-Butene-1,4-diol was subjected to oxymercuration-demercuration conditions according to a procedure reported by Brown, et al., or the hydration of olefins.[49,50,51] His work indicates the reaction to be almost quantitative under mild conditions with a broad variety of olefins. Although his report also indicates the product to be exclusively the Markovnikov hydration product with no observable rearrangements, significant rearrangements and other side reactions were observed when the reaction was applied under the same conditions to 2-butene-1,4-diol.

In principle, the reaction is similar to Reppe's method for BT synthesis[25,26] which has had extensive commercial application. Reppe hydrated 2-butyne-1,4-diol with aqueous mercuric sulfate and then reduced the intermediate to BT by catalytic hydrogenation over Raney nickel.

$$\begin{array}{c} CH_2OH \\ | \\ C \\ ||| \\ C \\ | \\ CH_2OH \end{array} \quad \underset{H_2O}{\overset{HgSO_4}{\xrightarrow{\hspace{1cm}}}} \quad \left[\begin{array}{c} CH_2OH \\ | \\ C - H \\ || \\ C - OH \\ | \\ CH_2OH \end{array}\right] \quad \longrightarrow \quad \begin{array}{c} CH_2OH \\ | \\ CH_2 \\ | \\ C = 0 \\ | \\ CH_2OH \end{array} \quad \overset{H_2}{\xrightarrow{\hspace{1cm}}} \quad BT$$
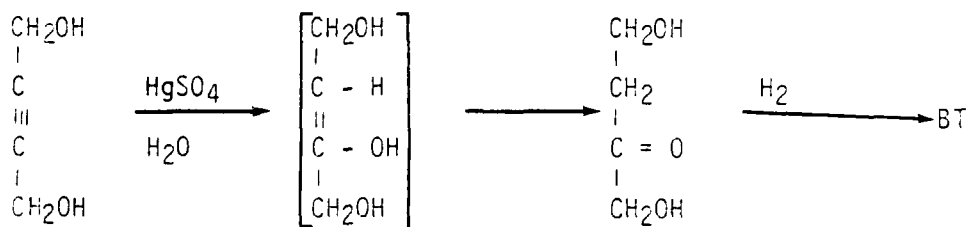
As anticipated, 2-butene-1,4-diol was found to react rapidly with mercuric acetate as evidenced by the disappearance of the intense yellow color of the salt within minutes after the addition of the olefin to a mixture of aqueous mercuric acetate and either tetrahydrofuran or methylene chloride at room temperature.

While olefin-mercuric salt addition compounds are generally thermally stable and easily isolated,[52] no attempt was made to isolate and characterize the mercurial of 2-butene-1,4-diol. It was allowed to react "in situ" with sodium hydroxide to effect the replacement of acetate by hydroxyl groups. After subsequent reduction of the mercurial with alkaline sodium borohydride, GC analysis indicated both the aqueous and organic layers to contain predominantly 1-butene-3,4-diol along with small amounts of BT, 1,2,3-butanetriol, and 2-butene-1,4-diol. Obviously something other than the anticipated reaction had occurred.

The 1-butene-3,4-diol was initially identified erroneously as 1,2-butanediol which has a very similar GC retention time in a Tenax column. Subsequent work showed the material to be 1-butene-3,4-diol, which is more understandable as olefins are not normally reduced by sodium borohydride under the conditions employed.

A search of the literature indicated that the mercuric salt addition has been examined for only one other α-hydroxy olefin, allyl alcohol, $CH_2 = CHCH_2OH$.[53-56] Under appropriate conditions, $CH_2(OH)CH(OAc)CH_2HgOAc$ can be obtained, but unlike the mercurials of other olefins, it is not thermally stable and it is also rapidly decomposed by even traces of weak acids to regenerate the parent olefin.[53] Olefin regeneration is a standard reaction of mercurials but generally requires a substantial concentration of a strong acid such as hydrochloric acid.

Apparently in the reaction of 2-butene-1,4-diol with aqueous mercuric acetate, traces of acetic acid are either present or generated, and isomerization of the olefin occurs.

```
CH2OH              CH2OH             CH2OH                      CH2OH
 |                  |                 |                          |
CH     Hg(OAc)2    CH-OAc            CH-OAc      Hg(OAc)2       CH-OAc
 ||   ⇌            |           →      |          ⇌              |
CH                 CH - HgOAc         CH                        CH-OAc
 |                  |                 ||                         |
CH2OH              CH2OH             CH2            CH2-HgOAc

  I                  II                III                        IV
```
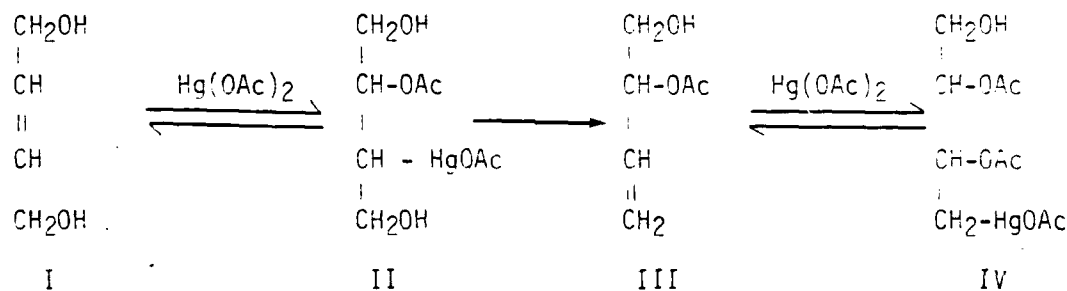
Subsequent saponification of III by sodium hydroxide produces 1-butene-3,4-diol, while the mercurials II and IV are reduced by alkaline sodium borohydride to yield BT and 1,2,3-butanetriol, respectively. Since the addition of mercuric salts is electrophilic,[57] there is probably little or no conversion of III back to II, and in the absence of any other competing reactions, extending the reaction time should increase the formation of IV. Analogous isomerizations for 2-butene-1,4-diacetate and dichloride in the presence of platinum, palladium, or copper catalysts have been reported to occur at elevated temperatures.[58-62]

To obtain additional information about the process, aqueous mercuric acetate was allowed to react with a four fold excess of 2-butene-1,4-diol. Samples were withdrawn periodically, saponified with sodium hydroxide, and analyzed by GC. Olefin peak areas were measured relative to an internal standard and are plotted versus time in Figures 10 and 11.

If there were no side reactions other than the olefin isomerization, the concentration of 1-butene-3,4-diol should steadily increase and the sum of the concentrations of the two olefins should drop to three-fourths of the original value when addition of mercuric acetate is complete. The limited data suggests that the increase in concentration of 1-butene-3,4-diol actually leveled off after about 4 hours. The sum of the olefin concentrations dropped to three-fourths its original value in a little less than an hour but then continued to drop at an increasing rate (Figure 12) suggesting the development

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HOURS	REL CONC
0.0	6.77
0.5	5.33
1.0	4.63
2.0	4.06
4.0	3.82
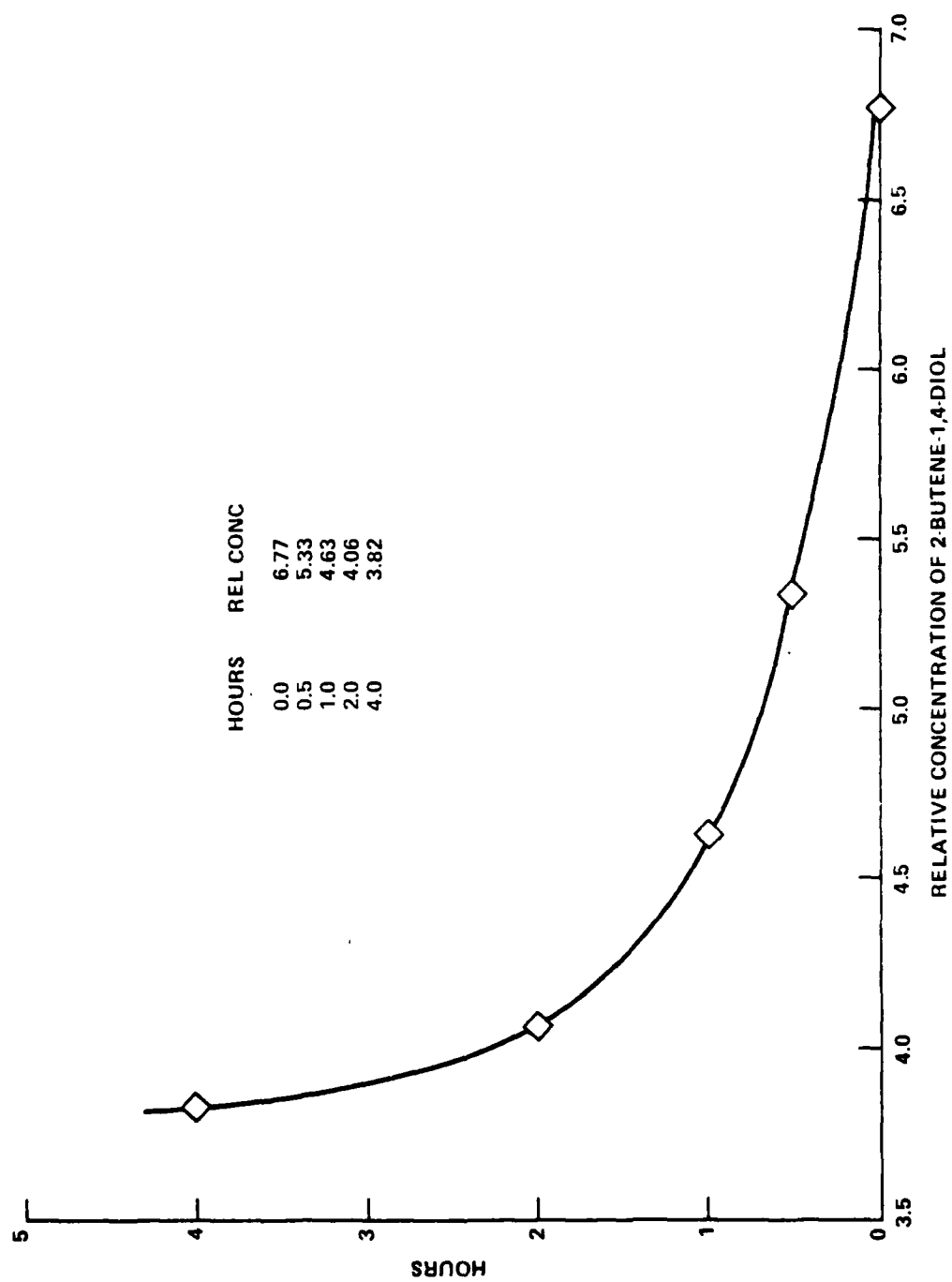
FIGURE 10. MERCURIC ACETATE INDUCED CHANGES IN CONCENTRATION OF 2-BUTENE-1,4-DIOL

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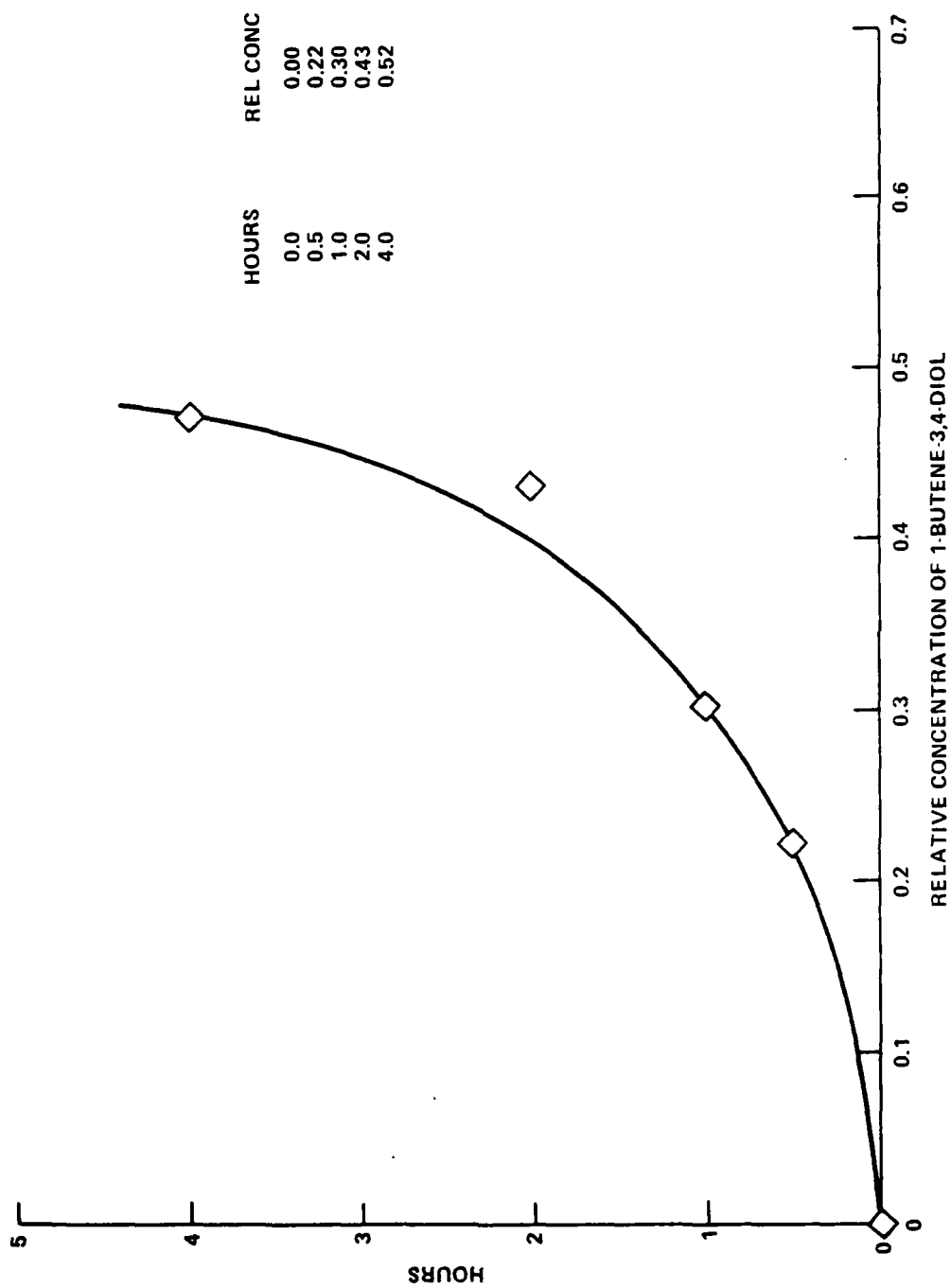| HOURS	REL CONC
0.0	0.00
0.5	0.22
1.0	0.30
2.0	0.43
4.0	0.52

FIGURE 11. MERCURIC ACETATE INDUCED CHANGES IN CONCENTRATION OF 1-BUTENE-3,4-DIOL

| HOURS	CONC
0.0	6.77
1.0	5.55
2.0	4.93
3.0	4.49
4.0	4.34
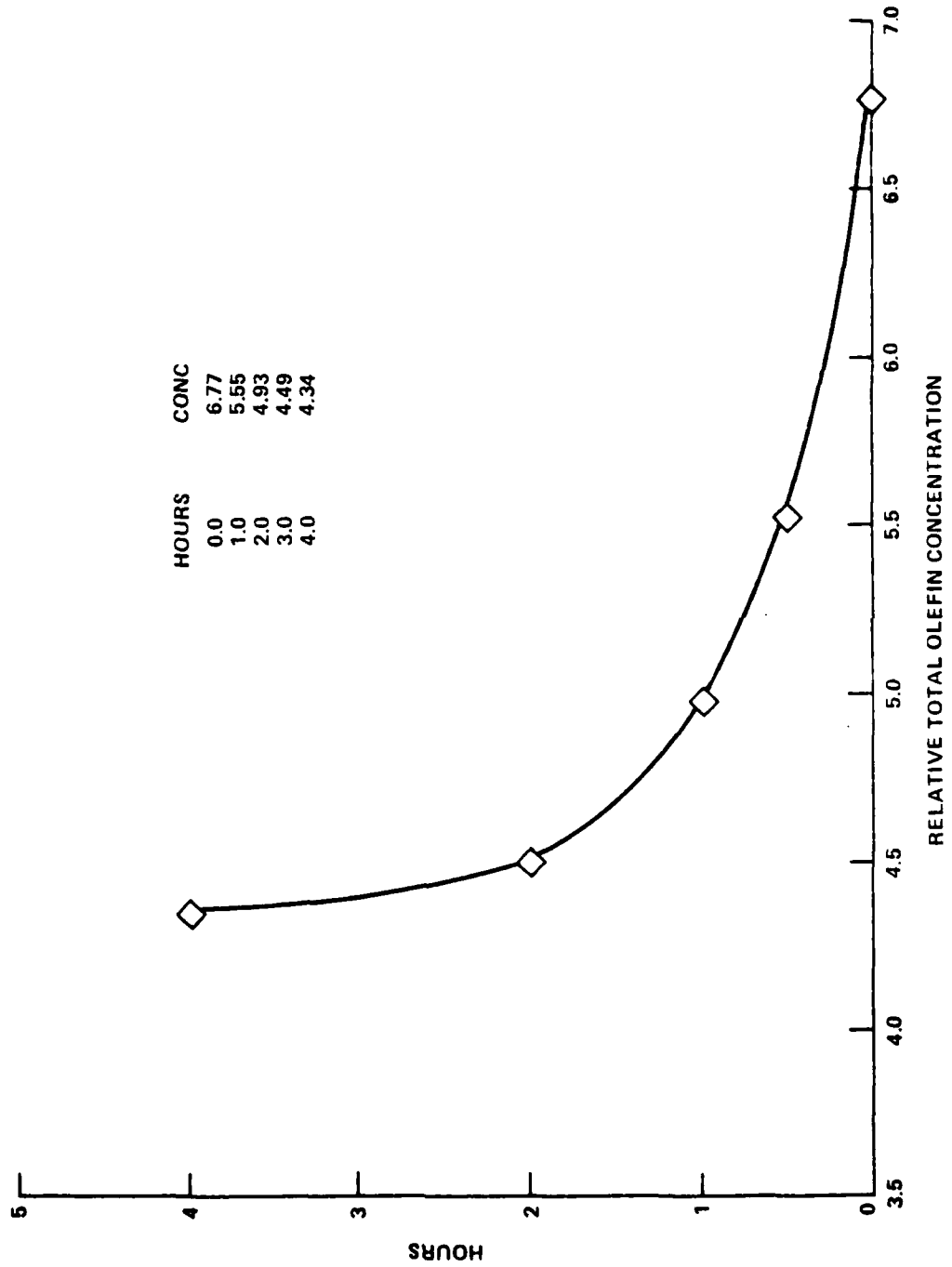
FIGURE 12. MERCURIC ACETATE INDUCED CHANGES IN TOTAL OLEFIN CONCENTRATION

RELATIVE TOTAL OLEFIN CONCENTRATION

HOURS

of a major secondary reaction. Furthermore, some triols were produced by
alkaline sodium borohydride reduction of an aliquot withdrawn after one half
hour, and no triol formation was observed from a sample reduced after 4 hours.
Apparently, the secondary reaction involved not only the olefins, but also the
mercurials II and IV.

A thorough study of the reaction was beyond the scope of the work objective
and not pursued. However, an examination of the literature on the reaction of
mercuric salts with allyl alcohol and other hydroxyl-containing olefins suggests
that the formation of cyclic or polymeric ethers may have occurred. Thus, allyl
alcohol has been reported to yield both the simple mercurial and a substituted
derivative of dioxane.[53-56]

$$
\begin{array}{ccc}
CH_2 & & CH_2\text{-HgOAC} \\
\| & \xrightarrow{Hg(OAc)_2} & | \\
CH & & CHOAC \\
| & & | \\
CH_2OH & & CH_2OH
\end{array}
\quad + \quad
\begin{array}{c}
CH_2-HgOAc \\
| \\
CH \\
\diagup \quad \diagdown \\
CH_2 \qquad O \\
| \qquad\quad | \\
O \qquad\quad CH_2 \\
\diagdown \quad \diagup \\
CH \\
| \\
CH_2 - HgOAc
\end{array}
$$
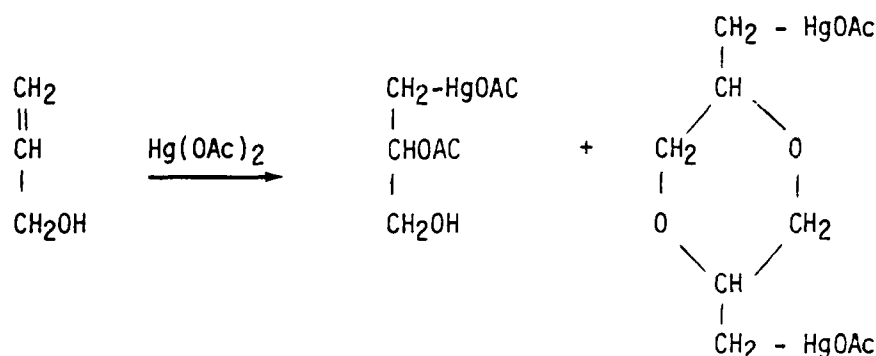
Other unsaturated substances containing hydroxyl groups have also been
reported to form ethers,[63-65] and allowing the simple mercuric salt addition
compounds to age, favors ether formation.[66]
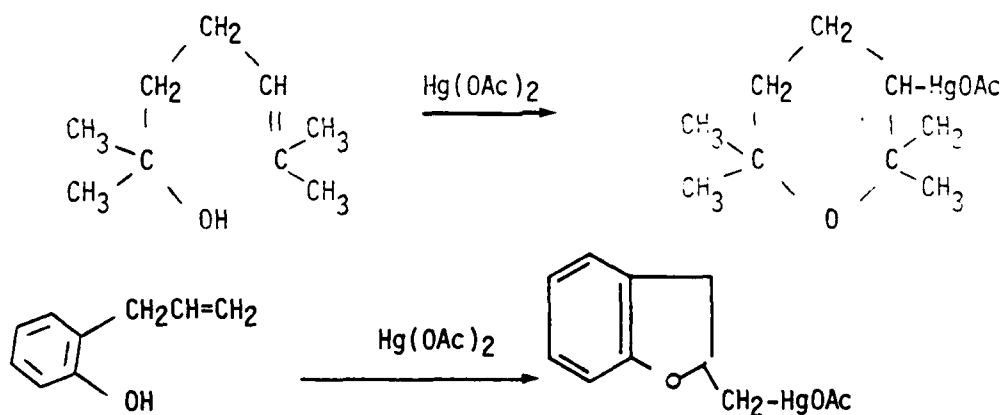
Although no further work is planned on this reaction, recommendations can
be made that might enable more successful olefin hydration. Isomerization of
2-butene-1,4-diol to 1-butene-3,4-diol may be reduced or avoided by alternately
neturalizing the mercuric salt solution until the basic salt just begins to
precipitate and then adding just enough olefin to redissolve it. The formation
of ethers may be inhibited by running the reaction below 10°C and by not allowing
the mercurial to age for longer than about one half hour before reducing it with
alkaline sodium borohydride.

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HYDROBORATION/OXIDATION OF 2-BUTENE-1,4-DIOL

$$HOCH_2CH \underset{HOCH_2CH}{\overset{\|}{}} \xrightarrow{MBH_4 + BF_3} \left(\underset{HO-CH_2-CH_2}{\overset{HO-CH_2-CH-}{|}}\right)_3 B \xrightarrow{H_2O_2} BT$$
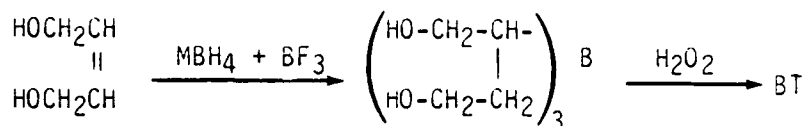
M = Li, Na

Relatively pure BT was synthesized by a technique described by Zweifell and Brown for the hydration of olefins under mild conditons.[67] Thus, 2-butene-1,4-diol in ethyl ether reacted at room temperature with excess diborane which was generated "in situ" by addition of boron trifluoride etherate to either lithium or sodium borohydride. A substantial excess of d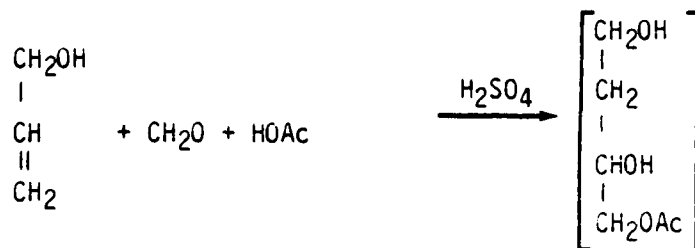iborane was generated in order to accommodate the formation of boric esters from the free hydroxyl groups. Other than necessitating a larger amount of diborane, this side reaction
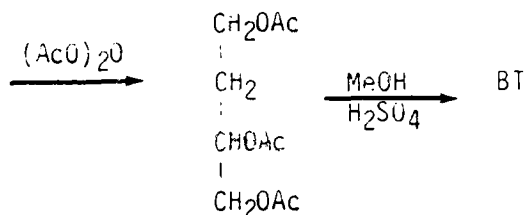
$$3ROH + BH_3 \longrightarrow (RO)_3B + 3H_2$$

does not interfer with the hydroboration. Less boron trifluoride etherate was required with lithium borohydride than with sodium borohydride as the by-products are lithium fluoride and sodium fluoroborate, respectively. Since an additional disadvantage of sodium borohydride is its insolubility in ether, ten mole percent of dry zinc chloride was added to catalyze the reaction with boron trifluoride. Excess diborane was destroyed by addition of water, which caused foaming and refluxing of the ether. The intermediate organoborane was then oxidized to BT by the addition of ethanolic potassium hydroxide and hydrogen peroxide. The ether layer was then stirred over calcium hydride until it no longer gave a positive test for peroxides with dichromate.[68] An 81 percent yield of BT was obtained using lithium borohydride and a 77 percent yield was obtained using the less expensive sodium borohydride.

The hazard of producing the peroxide of ethyl ether could be avoided by employing another solvent, such as anhydrous diglyme, triglyme, benzene, or toluene. Boron trifluoride etherate can also be replaced in hydroboration reactions with other acids, such as sulfuric acid, anhydrous hydrogen chloride, gaseous boron trifluoride, or aluminum chloride. Modifying the reaction conditions may also give some advantages to using hydrides other than lithium or sodium borohydride, such as potassium borohydride or lithium aluminum hydride. Such modifications should be examined before scale-up is considered.

CONDENSATION OF ALLYL ALCOHOL, FORMALDEHYDE, AND ACETIC ANHYDRIDE

$$\underset{CH_2}{\overset{CH_2OH}{\underset{\|}{\overset{|}{CH}}}} + CH_2O + HOAc \xrightarrow{H_2SO_4} \begin{bmatrix} CH_2OH \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ CH_2OAc \end{bmatrix}$$

41

$$(AcO)_2O \longrightarrow \begin{array}{c} CH_2OAc \\ | \\ CH_2 \\ | \\ CHOAc \\ | \\ CH_2OAc \end{array} \quad \xrightarrow[H_2SO_4]{MeOH} \quad BT$$

The cheapest practical method for the synthesis of BT may be the condensation of allyl alcohol, formaldehyde, and acetic anhydride in the presence of sulfuric acid. Based on an overall yield of 50 percent, the raw materials would cost approximately $0.90 per pound of BT.

Experimental conditions were developed and studied by the U. S. Rubber Company in 1948,[31,32] and their data indicated the method to be suitable for scale-up. Their procedures were re-examined as a part of this program. No significant difficulties were encountered, and their data were fully confirmed.

In the procedure followed, a solution of allyl alcohol and acetic anhydride was added to a mixture of paraformaldehyde, acetic acid, and sulfuric acid. The mixture was maintained at a temperature of 70 to 75°C for several hours, neutralized with sodium carbonate, filtered, and distilled.

The temperature of the mildly exothermic reaction can be easily maintained at the recommended 70 to 75°C, without external heating or cooling, by adjusting the addition rate of reactants to about 2 ml per minute on a 3 mole scale. Larger scale reactions or external cooling should permit higher feed rates. Higher temperatures can promote undesirable side-reactions and lower the yield.

Foaming during the sodium carbonate neutralization occurs but can be easily controlled by adding the carbonate in small increments. Should it present a problem in a large scale reaction, neutralization could be done, at least in part, with 50 percent sodium hydroxide, or anti-foaming agents might be added.

There was some difficulty in filtering the slimmy precipitate after the neutralization step, but this was greatly reduced by addition of diatomaceous earth and could be avoided on a larger scale by alternate solid/liquid separation techniques, such as continuous centrifugation. Incomplete removal of solids interferes with subsequent distillation of the solution and can promote super-heating, charring, and low yields.

A 50 percent yield of 1,2,4-butanetriol triacetate was obtained, which was the same as that reported by the U. S. Rubber Company. It had an IR spectrum identical to that obtained for the triacetate prepared by acetylation of BT with sodium acetate and refluxing acetic anhydride. The refractive index of the triacetate prepared by the two methods was

$$n_D^{25} \; 1.4349 \text{ and } n_D^{24} \; 1.4326, \text{ respectively.}$$
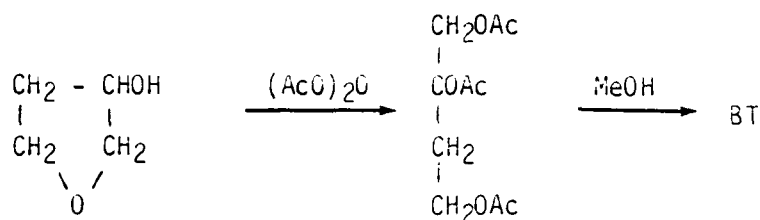
As discussed in another section of this report, 3-hydroxytetrahydrofuran also yielded BT triacetate having a refractive index of

$$n_D^{24} \ 1.4341$$

and an IR identical to those of the previous materials.

Acid catalyzed alcoholysis of the triacetate with refluxing methanol yields BT in about 90 percent conversion.[31]

CLEAVAGE OF CYCLIC ETHERS

```
                              CH2OAc
                               |
 CH2 - CHOH     (AcO)2O        COAc        MeOH
  |     |       ------->        |          ------->     BT
 CH2   CH2                     CH2
   \  /                         |
    O                          CH2OAc
```

The triacetate of BT was obtained in about 60 percent yield by refluxing 3-hydroxytetrahydrofuran (3-HTHF) with acetic anhydride for 3 hours in the presence of catalytic amounts of pyridine and sulfuric acid. The reaction conditions were identical to those described for the cleavage of tetrahydrofuran.[69,70] Alternately, the cleavage with acetic anhydride could have been effected by refluxing in the presence of zinc chloride or other catalysts.[71-75] 1,2-Epoxy-4-butanol should undergo a similar ring-opening acetylation to yield BT triacetate, but under more mild conditions than 3-HTHF.

After neutralization of the acetylation mixture with sodium bicarbonate and extraction with chloroform, vacuum distillation yielded BT triacetate having an IR spectrum identical to that of material prepared by acetylating BT with sodium acetate and refluxing acetic anhydride. The IR spectrum was also identical to that of the product obtained by the condensation of allyl alcohol, formaldehyde, and acetic anhydride as described in another section of this report. Refractive indexes of the three samples of BT triacetate are

$$n_D^{24} \ 1.4341, \ n_D^{24} \ 1.4326, \ \text{and} \ n_D^{25} \ 1.4349, \ \text{respectively.}$$

Alcoholysis of the triacetate with acidic methanol to yield BT in about 90 percent conversion is described elsewhere.[31]

Ring cleavage reactions were also examined as a technique to obtain partially nitrated butanetriols which would be useful in any future work on the aging mechanisms of propellants containing BTTN. Although an attempt to open the 3-HTHF ring with dilute nitric acid and ammonium nitrate at room temperature was unsuccessful, similar conditions have been used to cleave the more reactive epoxide ring[76-82] and should be applicable to 1,2-epoxy-4-butanol. As

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increasing the dielectric constant of the reaction medium tends to favor an SN_2 attack at the more alkylated epoxide carbon, the ratio of the isomeric nitratodiols can be varied.

$$
\begin{array}{c}
CH_2 \\
| \quad \diagdown \\
CH \quad O \\
| \quad \diagup \\
CH_2 \\
| \\
CH_2OH
\end{array}
\xrightarrow{\quad HNO_3 \quad}
\begin{array}{c}
CH_2\text{-}ONO_2 \\
| \\
CH\text{-}OH \\
| \\
CH_2 \\
| \\
CH_2OH
\end{array}
\quad + \quad
\begin{array}{c}
CH_2\text{-}OH \\
| \\
CH\text{-}ONO_2 \\
| \\
CH_2 \\
| \\
CH_2\text{-}OH
\end{array}
$$

44
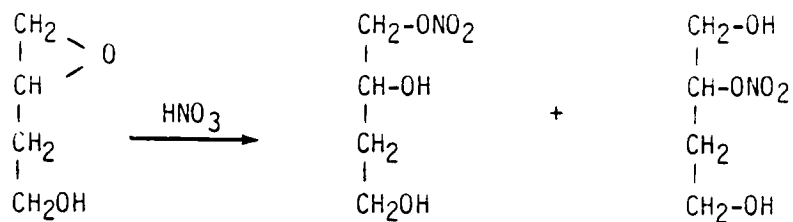
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NOMENCLATURE

BASF	Badische Anilin und Sodafabrick A. G.
BT	1,2,4-Butanetriol
BTTN	1,2,4-Butanetriol Trinitrate
GAF	General Aniline and Film Corporation
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HPLC	High Pressure Liquid Chromatography
3-HTHF	3-Hydroxytetrahydrofuran
IR	Infrared
KI	Potassium Iodide
MTN	Metriol Trinitrate
NC	Nitrocellulose
NG	Nitroglycerin
NOSIH	Naval Ordnance Station, Indian Head
OAc	Acetate
RI	Refractive Index
UV	Ultraviolet

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